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Synthesis, characterization and applications of magnetic multimetallic oxide nanocrystals

by

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ABSTRACT

Synthesis, characterization and applications of magnetic multi-metallic oxide nanocrystals

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Nanotechnology has had a great impact in several industries such as medical and electronics, and more recently in the oil and gas industry. In particular, magnetic nanoparticles are receiving great attention in the oil and gas industry because of their capability to enhance down-hole imaging. Ferrites are selected for this kind of applications because of the magnetic properties they exhibit such as high magnetic susceptibilities and high saturation magnetization. These properties could enhance the resolution of currently used geophysical techniques for imaging oil and gas reservoirs or increase the negative contrast in magnetic resonance imaging (MRI).

The Colvin group is well known for the synthesis of monodisperse ferrite nanocrystals, in particular Fe₃O₄. The research presented in this dissertation extends the previous works and shows the synthesis and physical characterization of spinel ferrites (MFe₂O₄, M= Mn²⁺, Co²⁺, Ni²⁺, and Zn²⁺) with a narrow diameter distribution. A very stringent control of the composition and size of the nanocrystals is one of the achievements of this work (Chapter 4). By varying these parameters, size and
composition, we can tune the magnetic properties. In addition, characterization of their magnetic properties depending on their size, composition and distinctive surface areas is explored and discussed.

The effect of other phenomena such as aggregation on the magnetic properties of nanoparticles was also studied (Chapter 5). This effect becomes important when aggregation is controlled causing a significant enhancement on the magnetic properties. For this reason, the synthesis and characterization of controlled magnetic ferrite nanoclusters was investigated. Magnetic susceptibilities observed in ferrite nanoclusters were much higher than any commercial nanomaterial available and synthesized isolated spinel ferrites.

Finally in Chapter 6, we explore the use of nanomaterials herein prepared for several applications, including magnetic separation, MRI contrast agents and contrast agents for down-hole imaging for the oil and gas industry. We utilize magnetic separation as a tool to separate magnetic materials based on composition of nanoparticles. For MRI contrast agents, doping of metals for Fe$^{2+}$ ions, size and aggregation of nanoparticles were found to significantly influence the MRI signal. Lastly, synthesized magnetic nanoparticles were found to have magnetic susceptibilities three times higher in solution and powders than any commercially available nanomaterial. Due to these high magnetic susceptibilities they could have great potential for down-hole imaging in the oil and gas industry.
First and foremost I want to thank my advisor Dr. Vicki Colvin for all her guidance in the Ph.D. pursuit. I appreciate all her contributions of time, ideas and funding to make my Ph.D. experience productive and stimulating. She has been an excellent example of a successful woman chemist and professor. I would also like to thank Prof. Matteo Pasquali and Prof. Michael Wong for participating as my thesis committee.

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<tr>
<td>AEC</td>
<td>Advanced Energy Consortium</td>
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<tr>
<td>BET</td>
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<tr>
<td>Oe</td>
<td>Oersted</td>
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<tr>
<td>PAA</td>
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<td>2-acrylamido-2-methylpropane sulfonic acid-(\text{co})-lauryl acrylate</td>
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<td>-------------</td>
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<tr>
<td>SI</td>
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<td>SQUID</td>
<td>Super Quantum Interference Device</td>
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In recent years, magnetic nanoparticles have been intensively studied due to their fundamental scientific significance and high applicability. \cite{1,2} A review of the properties of iron oxide nanocrystals properties and their current and potential applications is presented herein.

1.1. Magnetism

The study of magnetism began with magnetite as the first naturally occurring magnetic material known to man, the first magnetite deposits being found in what today is modern Turkey. One significant invention at that time was the mariner’s compass where it was observed that a piece of magnetite would float on water and would rotate until it was pointing towards north and south allowing for navigation
means other than by stars alone. It was not until several centuries later that the next major breakthrough came when Hans Christian Oersted discovered that an electric current produced a magnetic field. Oersted’s discoveries led to the discovery of the first electromagnet opening the gates to the initiation of an in depth understanding and creation of magnetic materials.³

Magnetic properties of materials involve are based on the magnetic dipole moment from the electrons of single atoms and the magnetic interactions between the atoms.⁴ The origin of magnetic moments comes from the orbital motion of an electron around the nucleus (Figure 1-1A). The electron could be considered to be a small current loop producing a small magnetic field with a resultant magnetic moment along its axis of rotation.⁵ Additional, magnetic moment also arises from the spin of electrons which are directed along the spin axis (Figure 1-1B).

![Diagram of Magnetic Moment](image)

**Figure 1-1. Magnetic moment of a magnetic material**
(A) Magnetic moment associated with an orbiting and (B) spinning electron. Taken from reference 4.
Magnetic materials consist of the sum of the interactions of the individual magnetic constituents. These magnetic moments are associated with a vector quantity which could be parallel to the axis of spin or perpendicular to the orbit plane. The total magnetic moment of an atom is given by the sum of all electronic moments.

Magnetic materials can be classified as diamagnetic or paramagnetic. Diamagnetism is a weak form of magnetism where all magnetic moments are aligned in such way that they cancel one another, with no net magnetic moment in the atoms, hence often referred to as being non-magnetic. When an external field is applied to diamagnetic materials, the induced magnetization would be pointing in the opposite direction as the applied field. Therefore, diamagnetic materials tend to repel applied fields. Atoms that have completely filled orbitals develop this type of magnetism. For example, all inert gases or compounds such as H₂O and NaCl possess such magnetic behavior. Magnetic susceptibility of diamagnetic materials is very small and negative. Interestingly, this ability of diamagnetic materials to be repelled by magnetic fields have led to the levitation of small animals such as frogs.

Paramagnetic materials have magnetic moments randomly oriented as a result of thermal agitation. Atomic orbitals are not completely filled leading to an overall magnetic moment. When an external field is applied, magnetic moments align with the field. Some of the materials can exhibit a remnant magnetization, meaning that when an applied magnetic field is removed, an overall magnetic
moment still exists. Paramagnetic materials can be further classified as ferromagnetic, antiferromagnetic and ferrimagnetic materials.

Ferromagnetic materials exhibit net magnetization without the continued application of an external field. Without any magnetization each domain is randomly oriented (Figure 1-2A). These materials saturate at very high magnetic fields where the internal domains are aligned with increasing magnetic field. Maximum magnetization or saturation magnetization is achieved when all magnetic dipoles are aligned. When the external magnetic field is applied, the magnetic dipoles remain aligned and keep an overall magnetization. Metals such as nickel, iron, and cobalt develop this type of magnetic behavior.

Like ferromagnetic materials, antiferromagnetic materials have no magnetization in the absence of an applied external magnetic field. The main difference arises in that when an external field is applied, an antiparallel alignment of magnetic moments occurs leaving no net magnetization (Table 1-1).

Finally, in ferrimagnetic materials, the magnetic domains tend to align in an antiparallel fashion but due to the magnetic structure, it is an unequal cancellation of magnetic moments, leading to an overall net magnetization. Magnetite, the oldest known magnetic material exhibits this type of magnetic behavior, where all atoms in A-sites are aligned in one direction and atoms in the B-sites are aligned in the opposite direction from the A-sites. Since the magnetic moment of the atoms in the A-sites is larger than atoms in B-sites, moments do not cancel each other and, a net magnetization occurs.
Ferromagnetic and ferrimagnetic materials are composed of different regions called domains in which all magnetic moments in each are aligned in the same direction (Figure 1-2A). Magnetic domains are separated by domain walls. For a typical crystalline specimen, there would be more than a single domain. As magnetic field is applied (H) domains start changing in shape and size through the movement of the domain walls until saturation magnetization (Ms) is reached (Figure 1-2B).

![Diagram of Magnetic Domains and Domain Walls](image)

**Figure 1-2. Magnetic behavior of ferromagnetic or ferrimagnetic material.** (A) Magnetic domains in a ferromagnetic or ferrimagnetic material. In each domain all dipoles are aligned in the same direction and (B) magnetic behavior of a ferromagnetic or ferrimagnetic material.

Table 1-1 shows a summary of all types of magnetism with their corresponding description of their magnetic behavior.
<table>
<thead>
<tr>
<th>Type</th>
<th>Atomic/ Magnetic behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetism</td>
<td>Atoms possess no magnetic moment</td>
</tr>
<tr>
<td>Paramagnetism</td>
<td>Atoms have randomly oriented magnetic moments</td>
</tr>
<tr>
<td>Ferromagnetism</td>
<td>Magnetic moments align parallel to each other</td>
</tr>
<tr>
<td>Antiferromagnetism</td>
<td>Magnetic moments align anti-parallel to each other</td>
</tr>
<tr>
<td>Ferrimagnetism</td>
<td>Magnetic moments align parallel and anti-parallel</td>
</tr>
</tbody>
</table>

Table 1-1. Summary of magnetic behavior of magnetic moments.
Table summarizes the magnetic behavior of magnetic materials, the arrangement of magnetic moments and the hysteresis behavior. Adapted from reference 6.

Temperature is an important factor that needs to be considered for ferromagnetic, antiferromagnetic and ferrimagnetic materials. As temperature is increased, random orientation of the magnetic moments would occur and moment rotation would be much harder to achieve.\textsuperscript{10} This behavior would produce a decrease in saturation magnetization until it reaches zero. The temperature at where magnetization reaches zero is called Curie temperature (T\textsubscript{c}).\textsuperscript{11} Above this temperature the material becomes paramagnetic and loses the ability to exhibit a remnant magnetization. For example, for magnetite the Curie temperature is around 575 °C. Figure 1-3, shows the decay in magnetization as temperature is increased for magnetite.
Figure 1-3. Saturation magnetization as a function of temperature for magnetite.
Curie temperature for magnetite materials which is the temperature at which materials reaches zero magnetization and at temperatures above it the material becomes paramagnetic.

As an external magnetic field is applied for ferromagnetic and ferrimagnetic materials below $T_c$, saturation magnetization ($M_s$) is reached when all magnetic dipoles are aligned. The slope of this first curve is the initial magnetic susceptibility ($\chi$) which is related to magnetic permeability ($\mu$). Magnetic susceptibility is a measurement done in order to identify the degree to which the material can be magnetized. Once saturation magnetization is reached, the field is applied in the opposite direction and most of the time producing a hysteresis effect in these types of magnetic materials. They experience this effect due to the magnetic domain
walls and grain boundaries. This would produce a residual field at zero magnetization, which is called remanence ($M_r$). In order to reduce the retained magnetization back to zero a field in opposite direction to the original needs to be applied. This field is called coercive field ($H_c$). Figure 1-4 shows a typical hysteresis loop for ferro- or ferromagnetic materials which presents important information that is usually gathered from the magnetic curve.

![Hysteresis Loop Diagram](image)

**Figure 1-4. Hysteresis loop**
Schematic representation of a hysteresis loop of a ferromagnetic material showing saturation points, retentivity points and coercivity points. Adapted from reference 12.

Moreover, there is a special condition of ferro- or ferri-magnetic particles referred to as superparamagnetic particles. This phenomenon occurs when there is a reduction in size of the particles. Usually, particles in the bulk are in the multi domain regime, where domains are separated by domain walls to reduce
magnetostatic energy. As size of particles decreases, particles develop a single domain (Figure 1-5). For single domain particles, all magnetic spins are aligned in the same orientation as the magnetic field is applied. In this regime, there is a larger coercive field because of all magnetic moments being oriented in the same direction (Figure 1-5). Consequently, as size further decreases below the point of stable single domain particles reach the superparamagnetic regime. In this regime, there is a lack of coercivity which makes them ideal for many applications such as classical magnetic storage devices. The transition of these three regimes (from multi domain to single domain to superparamagnetic domain) depends on the size, compositions and shape of the material. For superparamagnetic particles, it is easier for the thermal agitation to change the orientation of the magnetization spontaneously in the absence of an external field. This phenomenon happens from the thermal fluctuations within the particles equal or greater than the energy barrier producing rapid flipping of the nanoparticle magnetic moments. Superparamagnetism occurs above the blocking temperature which is associated with the energy barrier and depends on the measuring time which can vary from 100 to 10^{-8} s. The magnetic response comes from the relative difference between the measuring time and the relaxation time. Nanoparticles are defined as superparamagnetic if the measuring time is greater that the relaxation time. Nonetheless, if the relaxation time is greater than the measuring time the nanoparticles are in a blocked regime. Blocking temperatures can be experimentally obtained from ZFC-FC curves which are described in Chapter 2. Superparamagnetic particles are of great interest in applications such as magnetic resonance imaging (MRI) or any imaging
application and drug delivery because of the strong response in an applied magnetic field combined with the lack of remnant magnetization which would prevent their use in these systems.  

![Figure 1-5. Effect of particle size on coercivity.](image)

The simplest and most common method of describing magnetic properties of superparamagnetic materials is the Langevin equation (Equation 1-1) which is dimensionless. The Langevin equation assumes that there are non-interacting nanoparticles and the sample is isotropic. Therefore, the magnetic moment of every single particle will be energetically the same.
\[ L(x) = \left( \cot x - \frac{1}{x} \right) \quad x = \frac{\mu H}{k_B T} \]

**Equation 1-1. Langevin function**

The magnetization of a superparamagnetic nanoparticle as a function of an external field \( H \) and temperature \( T \) is

\[ M = \frac{NM_0V}{V} \left( \cot x - \frac{1}{x} \right) = M_s L(x) \quad x = \frac{M_0 \nu_0 H}{k_B T} \]

**Equation 1-2. Magnetization of magnetic nanoparticles**

where \( N \) is the number of particles, \( \nu \) the volume of a particle, \( V \) the volume of the system, \( \mu_0 \) is the permittivity of vacuum, \( M_0 \) the bulk saturation magnetization and \( L(x) \) the Langevin function.

### 1.2. Multi-metal oxide nanocrystals

Magnetite, the most common magnetic iron oxide material, is a type of spinel ferrite.\(^{23}\) Magnetic spinels have the general formula \( \text{MFe}_2\text{O}_4 \) where \( \text{M} \) is a divalent metal ion. Spinel ferrites are classified as normal spinel, inverse spinel and mixed spinel.\(^{24}\) Magnetite has an inverse spinel structure with oxygen atoms forming a cubic close-packed arrangement with \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) at two different crystallographic sites (Figure 1-6A).\(^{23,24,25}\) These two crystallographic sites have tetrahedral and octahedral oxygen coordination. The tetrahedral sites are known as A-sites and octahedral sites known as B-sites. In the A-sites metal cations are tetrahedrally
coordinated to oxygen atoms and B-sites are octahedrally coordinated. These structural features are crucial to the magnetic properties of the spinels. Regarding the magnetic interaction between atoms of A-sites and B-sites atoms, there is a small interaction between A-A and B-B. In contrast, there is a much stronger interaction between A and B sites leading to the observation of ferromagnetic behavior as described in Table 1-2. For magnetite, half of the octahedral sites are occupied by Fe$^{2+}$ cations and the tetrahedral sites and remaining octahedral sites are occupied by Fe$^{3+}$ (Figure 1-6B).

![Crystal structure of magnetite and splitting of d orbitals](image)

**Figure 1-6.** **Crystal structure of magnetite and splitting of d orbitals.** (A) Magnetite crystal structure and (B) schematic of the splitting of 5d orbitals in tetrahedral and octahedral coordination of magnetite. Adapted from reference 25.

In addition, there are other types of spinel ferrites incorporating other metal cations which will change the magnetic properties and potential for many applications. For other spinel ferrites structures, MFe$_2$O$_4$ (M=metal cation, M$^{2+}$) such as normal spinel ferrites, A-sites are occupied by M$^{2+}$ and B- sites are occupied by
Fe\textsuperscript{3+}. For example, Table 1-2 shows zinc ferrite as a normal spinel where tetrahedral sites are occupied by zinc ions and octahedral sites are occupied by Fe\textsuperscript{3+} ions. Zinc is a diamagnetic atom (lack unpaired electrons) which cannot interact with the unpaired spins on Fe\textsuperscript{3+}.

Lastly, mixed spinel structures A-sites and B-sites are occupied by both M\textsuperscript{2+} and Fe\textsuperscript{3+}.\textsuperscript{26, 27} Table 1-2 shows the arrangement of ions for a Mn-Zn ferrite. Zinc ions prefer to go to the tetrahedral sites and half Fe\textsuperscript{3+} ions occupy the rest of the tetrahedral sites available. The rest of Fe\textsuperscript{3+} ions occupy octahedral sites. The iron ions from A and B sites interact in an antiparallel manner with each other. Therefore, neutralizes one third of the Fe\textsuperscript{3+} ions in the octahedral sites leaving large magnetic moment from iron ions. Additionally, we take into consideration the magnetic moment of the other M\textsuperscript{2+} which is Mn\textsuperscript{2+} and fills the rest of the octahedral sites available. As a result, this leaves a large total magnetic moment in mixed ferrites.
<table>
<thead>
<tr>
<th>Spinel type</th>
<th>A (T_d sites)</th>
<th>B (O_h sites)</th>
<th>Resultant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal (ZnFe_2O_4)</td>
<td>Zn^{++} --- Fe^{+++} ↓</td>
<td>Fe^{+++}</td>
<td>---</td>
</tr>
<tr>
<td>Inverse (Fe_3O_4)</td>
<td>Fe^{+++} ↓ Fe^{+++}</td>
<td>Fe^{++}</td>
<td>↑ ↑</td>
</tr>
<tr>
<td>Mixed (Zn_{0.5}Ni_{0.5}Fe_2O_4)</td>
<td>Fe^{+++} ↓ Fe^{+++}</td>
<td>Ni^{++}</td>
<td>↑ ↑</td>
</tr>
</tbody>
</table>

Table 1-2. Balancing the effect of composition for ferrite nanoparticles.
Balancing the effect of composition in different spinels crystalline structures. Adapted from reference 26.

The site preference of ions depends on the ionic radii of ions, the size of the interstices, temperature and the orbital preference for coordination. For example, divalent ions are generally larger than trivalent ions due to the larger charge which produces greater electrostatic attraction. Therefore, divalent ions usually occupy octahedral sites since these are much larger than tetrahedral. There are two exceptions ions for this rule, Zn^{++} and Cd^{++} which prefer to go into the tetrahedral sites because of their electronic configuration.

1.3. Nanomaterials for imaging applications

Recently, there has been an extensive increase in the number of studies aimed at understanding of the magnetic properties of nanomaterials.28 Magnetic
nanoparticles possess unique properties that make them suitable for many applications in the biomedical field.\textsuperscript{29,30,31} For example, two of the major challenges in this field is the early detection of diseases and the delivery of treatment at the right location with the correct dose.\textsuperscript{32,33,34} Magnetic nanoparticles can be synthesized with high monodispersity, such that their magnetic properties can be optimized and they can be functionalized for biocompatibility to combine therapeutic and diagnostics capabilities.\textsuperscript{31,35} Figure 1-7 shows varying applications where magnetic nanoparticles could have great potential. The surface of magnetic nanoparticles can be modified for a desired application (Figure 1-7A). Magnetic nanoparticles can be directed to a targeting location by using a magnetic field or by injecting them in the appropriate location (Figure 1-7B). Once they reach their desired location, nanoparticles could be used as contrast agents such as MRI or other imaging techniques (Figure 1-7C). Also, due to their dynamic relation when an alternating magnetic field is applied could be used for hyperthermia or biosensing (Figure 1-7D). The nanoparticles could be functionalized to attach drugs or a gene and be released by an external stimulus such as temperature, pH or a magnetic field (Figure 1-7E). Finally, the magnetic nanoparticles could be moved through magnetic fields to allow for magnetic targeting, delivery and diagnostics (Figure 1-7F).\textsuperscript{36}
Figure 1-7. Applications of magnetic nanoparticles in the biomedical field.

(A) Surface modification of magnetic nanoparticles, (B) they can be guided to a desired location by applying a magnetic field, (C) can be utilized as contrast agents for MRI studies, (D) can be used for therapeutics or biosensing, (E) functionalization of the magnetic nanoparticle to attach and release biological molecules in the presence of an external stimuli and (F) by the application of an external field leads to applications such as magnetic targeting and drug delivery. Adapted from reference 36.

With all the aforementioned application of the existing medical applications one of the greatest potential for these superparamagnetic nanoparticles are in MRI contrast agent imaging.37 Much research has been performed in this area.38,39
1.3.1. Magnetic Resonance Imaging (MRI)

Magnetic resonance imaging is one of the most powerful non-invasive imaging techniques.\textsuperscript{40} Magnetic nanoparticles used as contrast agents for MRI increases the capability of differentiation between healthy and pathological tissues.\textsuperscript{41,42} Contrast agents for MRI are usually classified as T\textsubscript{1} or T\textsubscript{2} contrast agents. Superparamagnetic iron oxide nanoparticles are the first type of contrast agents that were used for MRI.\textsuperscript{42,43} These nanoparticles provide strong contrast for T\textsubscript{2} weighed images, whereas, typical contrast agents for T\textsubscript{1} weighed images are composed of Gd- based nanomaterials.\textsuperscript{44,45,46}

The term contrast comes from the signal differences between adjacent regions such as tissue and tissue, tissue and vessel and tissue and bone.\textsuperscript{47} MRI is based on the mechanism that results from the interaction between the contrast agents and water protons. The fundamental MRI principle comes from nuclear magnetic resonance (NMR) and the relaxation of proton spins (hydrogen atoms) when a magnetic field $B_0$, up to 2 T in clinical apparatus is applied.\textsuperscript{39} Hydrogen atoms are the most widely abundant in biological organisms and most sensitive nucleus. When a magnetic field is applied, protons aligned either parallel or antiparallel. After the alignment, the spins change in orientation of the rotational axis of protons under a specific frequency known as the Larmor frequency \textsuperscript{(}$\omega_0 = \gamma B_0$, where $\omega_0$= larmor frequency, $\gamma$= gyromagnetic ratio and $B_0$= magnetic field) (Figure 1-8A). The process in which the aligned protons return to their original state is called relaxation phenomenon. When a resonance frequency in the range of radio frequency range is
applied to the nuclei, protons absorb energy and align in an antiparallel fashion.\textsuperscript{47} Then, after the radio frequency signal is removed, the excited nuclei relax to a lower energy state, which is their initial state (Figure 1-8B). The relaxation phenomenon is categorized as longitudinal (M$_z$) or T$_1$ relaxation and transverse relaxation (M$_{xy}$) or T$_2$ relaxation. Longitudinal relaxation or T$_1$ happens when the decrease net magnetization recovers to its initial state (Figure 1-8C). T$_1$ is the time required for longitudinal magnetization to recover 63\% of the initial state. Whereas T$_2$ relaxation occurs when the induced magnetization on the perpendicular plane disappears from the dephasing of the spins (Figure 1-8D). T$_2$ is the time required for transverse magnetization to drop to 37\% of its initial magnitude.\textsuperscript{47}

\textbf{Figure 1-8. Principle of magnetic resonance imaging (MRI).} (A) Spins aligned to the magnetic field and precess under Larmor frequency, (B) magnetization of spins changes, (C) T$_1$ relaxation and (D) T$_2$ relaxation. Adapted from reference 48.
Contrast agents are used to improve the visibility of materials by altering the relaxation times. Relaxivity of an MRI contrast agents increases as follows

\[ R_i = \frac{1}{T_i} = \left( \frac{1}{T_i} \right)_0 + r_i C \]

**Equation 1-3. Relaxation rate of aqueous solution.**

where \( R_i \) is the relaxation rate, \( T_{i0} \) is the relaxation without a contrast agent, \( C \) is the concentration of contrast agents (mM) and \( r_i \) is the relaxivity (s\(^{-1}\) nM\(^{-1}\)) . For \( T_1 \) contrast agents they usually increase \( r_1 \) and \( r_2 \) by the same amount. \( T_1 \) contrast agents show a positive contrast. In contrast, \( T_2 \) contrast agents there is a greater increase in \( r_2 \) and \( r_1 \) and they are negative contrast agents.

Magnetic iron oxide nanoparticles are superparamagnetic nanoparticles, which have a similar behavior as paramagnetic materials and lose their magnetization in the absence of an external magnetic field while having a much higher magnetic moment. When a magnetic field is applied, they exhibit a strong magnetization inducing a heterogenous local magnetic field through which water molecules diffuse. They are mostly used to produce \( T_2 \) relaxation, which generates signal reduction on \( T_2^* \), weighed images. A common clinical application, which uses superparamagnetic iron oxide nanoparticles, is lymph node imaging. This application is used for accurate detection of tumor staging. Magnetic nanoparticles are transported to lymph nodes through lymphatic vessels (Figure 1-9A). Nanoparticles accumulate in normal nodes and produce significant susceptibility
effects, which generate a more sensitive detection of normal and malignant cells. This technique improves the diagnosis of metastatic tumors. Figure 1-9C shows the positive detection of lymph node metastases in patients with prostate cancer when superparamagnetic nanoparticles are used as contrast agents.

**Figure 1-9. Injections of superparamagnetic nanoparticles for MR enhancement.**
Injection of superparamagnetic iron oxide nanoparticles, (B) MR images of metastatic lymph node before injection and (C) MR images of metastatic lymph node after injection of magnetic nanoparticles. Adapted from reference 50.
1.3.2. Nanotechnology in oil and gas industry

As described above, nanotechnology has been of great interest in many different industries such as electronics, biomedical, environmental and more recently the energy sector. Nanotechnology has led to the development of unique materials with physical characteristics that cannot be compared to conventional materials, which can solve some of the major challenges the oil and gas industry is facing.\textsuperscript{51,52} Oil and gas reservoirs are porous and permeable rock formations which contain the desired hydrocarbon, and nanoparticles offer a distinctive advantage of manipulating a material being able to manipulate the chemical properties needed down-hole in a material which will not cause damage by plugging off these permeable channels where the oil and gas flow. Nanotechnology has many opportunities in different areas of oil and gas industry such as enhanced oil recovery, drilling, production, exploration and refining (Figure 1-10). Some proposed examples have been in the development tiny sensors that could be injected into the reservoirs, withstand harsh conditions underground and provide information about the reservoir characteristics.
Figure 1-10. Nanotechnology applications for upstream oil and gas.
Nanotechnology can be applied in several areas of the oil and gas industry such as exploration, drilling, enhance oil recovery, production and refining. Adapted from reference 51.

Currently, oil and gas exploration and production is facing some technical challenges because of changes in operational depth, the length of horizontal departure to maximize production, and the shape of wellbores and the complexity of drilling operations. The materials used for this application are also facing several challenges with the physical, chemical and thermal conditions present in down-hole environments where the pressured can exceed 30,000 psi and temperatures greater than 450°F have been encountered. Standard polymer and surfactant chemistries fail under these conditions and this is where nanotechnology...
could have great opportunities to make significant contributions to the oil and gas industry.

In a typical oil well, only 30-50% of the original oil in place is produced. These resources are still unrecovered and could be recovered if a better understanding of the physical and chemical properties of reservoir could be obtained. According to studies made by the U.S. Department of Energy (DOE) there is still 60-70% of oil which cannot be recovered with current techniques. Presently, current imaging techniques, besides seismic, have limited resolution and cannot penetrate deeply in a reservoir, making it challenging to determine the location of the remaining hydrocarbon deposits. By improving the electrical and electromagnetic imaging methods and coupling that data to revise reservoir simulations and models, a more economically viable well construction and field draining program can be obtained. The use of superparamagnetic nanoparticles has been investigated to serve as contrast agents for electromagnetic imaging of oil reservoirs.55,56 The major challenge of these nanoparticles would be that they possess a high initial magnetic susceptibility which would make it possible to generate signals under the application of a low external field.

For drilling applications, equipment could be made utilizing nanomaterials which could improve corrosion resistance, wear resistance, shock resistance and enhanced thermal conductivity.57,58,59 Furthermore, there has been an increased focus on the next generation of fluids referred to as “smart fluids” for drilling, stimulation and production which improves wettability alteration, advanced drag
reduction and sand consolidation.\textsuperscript{60,61} For example, Figure 1-11 shows the wetting behavior of nanoparticles when air bubble or droplet is added to a micellar solution (5 nm micelles with a hydrophilic surface and hydrophobic core) where it is observed the wetting edge in the space between the oil drop or air bubble and the solid surface. It seems that the micelles somehow get organize in the wetting edge. This generates osmotic component in the excess pressure which tries to separate the two interfaces and is directed towards the wedge component. The excess pressure causes further spreading of the solution and can be large enough to separate the oil droplet or air bubble form the solid surface.

\textbf{Figure 1-11. Wetting behavior of a solution of nanoparticles.}
Wetting edge was observed on the solution in the space between the drop or bubble and the solid surface when the air bubble or oil drops got in contact with the glass surface. Image taken from reference 60.
Enhanced oil recovery is also an area where nanotechnology could have a great impact. Some of the major problems that current techniques face are the high cost of injectants. For example, the solutions of alkaline injection and surfactant flooding. Also, possible corrosion of formation and the injectant loss as they flow through the reservoir. Nanoparticles could be used to solve some of these previously mentioned problems. Usually, the fluids that are injected for recovery have much lower viscosity than oil. Therefore, addition nanoparticles to a fluid solution could improve the viscosity of the injected fluid and as a result would improve the mobility of the fluid. This generates a more efficient oil recovery process.

Lastly, refining and processing is an area that faces several challenges such as limiting the emissions of sulfur and carbon dioxide (CO₂) and impurities in crude oil. Refineries are in need of having high yields but by consuming fewer resources such as steel, and CO₂. Nanotechnology has already been used in this area of the oil and gas industry where a mesoporous catalyst MCM-41 has been highly used for many chemical reactions in the refining process. Additionally, nanofilters and nanomembranes have been employed to remove toxic substances such as nitrogen oxides, sulfur oxides and many other impurities present in crude oil.

Nanoparticles offer many interesting advantages when compared to bulk materials due to the manipulation that can be achieved in the atomic level. The functionalization of the surface area of nanoparticles could help to make them more stable under the hostile conditions present underground. All of these characteristics
could potentially solve some of the major problems and challenges the oil and gas industry is facing.

1.4. Motivation

The Colvin Group is well known for the synthesis of monodisperse nanocrystals with an emphasis on iron oxides and the engineering of tailored surface coatings.\textsuperscript{62,63} These magnetic nanocrystals are well known to have great properties for many biomedical applications and more recently in oil and gas.\textsuperscript{57} Magnetic properties of these nanocrystals have been widely studied to completely understand the behavior of each system and apply these materials in an optimal application. Typically, superparamagnetic materials are the ones that are having a great impact in these previously mentioned areas due to the lack of magnetization they show in the absence of an external field. Magnetic nanomaterials show high magnetic response and behave as superparamagnetic are the ideal materials to use. In this work the following main objectives the will be addressed:

1. Understand the magnetic behavior of commercial materials provided from AEC. \textit{Chapter 3}

2. Design of magnetic nanoparticles and determine effect of size and composition on the magnetic properties. \textit{Chapter 4 and 5.}

3. Demonstrate potential applications for magnetic nanocrystals synthesized. \textit{Chapter 6.}
Chapter 2

Experimental section

2.1. Introduction

The synthesis of magnetic nanoparticles has been intensively studied, particularly for ferrites. These magnetic nanocrystals offer intrinsic properties in many different areas such as magnetic recording, environmental remediation, magnetic resonance imaging\textsuperscript{64,65}, bioseparation\textsuperscript{66} and drug delivery\textsuperscript{67}. Many synthetic methods such as hydrothermal, microemulsion, thermal decomposition and coprecipitation have been utilized by scientific community\textsuperscript{68,69,70}. The major drawbacks of many of these methods are that the nanocrystals produced lack of crystallinity and monodispersity, which could lead to a drastic change on their magnetic properties\textsuperscript{71}. Therefore, it is crucial to develop a synthetic route for controlled size and composition synthesis of these nanocrystals. Colvin et al. recently reported the synthesis of simple ferrite, Fe$_3$O$_4$, which consists of a non-
hydrolytic route, thermal decomposition route, which used iron oxide hydrated as the iron precursor.\textsuperscript{72} Hyeon et al. reported the synthesis of highly monodisperse nanocrystals which used iron oleate as the metal precursor.\textsuperscript{73} Sun et al. synthesized iron oxide nanocrystals from the decomposition of metal acetylacetonates.\textsuperscript{23,74} From all of these studies, it was discovered that the intermediates, iron carboxylates, which are produced through the reaction of an iron salt with oleic acid are the actual precursors for the formation of the nanocrystal.\textsuperscript{73,75} Based on this analysis, a method was developed to utilize abundant and inexpensive metal chloride salts can be used to generate the iron carboxylate and through pyrolysis of the organic material form the nanocrystal. This novel method has been utilized for the synthesis of controlled composition and monodisperse spinel ferrites MFe$_2$O$_4$ ($M$= Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$).

\section*{2.2. Experimental methods}

\subsection*{2.2.1. Chemicals}

\textit{Synthesis of nanocrystals.} Iron (III) chloride hexahydrate (FeCl$_3$ ·6H$_2$O, reagent grade, 97%), iron (II) chloride manganese (II) chloride tetrahydrate (MnCl$_2$·6H$_2$O, 98%), nickel (II) chloride hexahydrate (NiCl$_2$ ·6H$_2$O, 98%), zinc chloride (ZnCl$_2$, reagent grade, 97%), cobalt (II) chloride hexahydrate (CoCl$_2$ ·6H$_2$O, 98%), oleic acid (OA, technical grade, 90%), 1-octadecene (ODE, technical grade, 90%), poly(ethylene glycol) (H(OCH$_2$CH$_2$)$_n$OH, PEG, Mw=2000 and 500),
polyvinylpyrrolidone \((\text{C}_6\text{H}_9\text{NO})_n\), PVP, Mw= 29,000 and 40,000), poly(acrylic acid) (PAA, Mw= 1,800 and 450,000), ethylene glycol (HOCH\text{2}CH\text{2}OH, 99.8%), diethylene glycol ((HOCH\text{2}CH\text{2})_2\text{O}, ≥ 99.0%) and sodium acetate (CH\text{3}COONa, > 99%) were purchased from Sigma Aldrich. Ethanol 200 and 190 proof (95%, KOPTEC) was purchased from VWR. Hexanes (certified ACS grade) and acetone (certified ACS grade) were acquired from Fisher Scientific. Lastly, sodium oleate was purchased from Pfaultz & Bauer.

*Surface modification of nanocrystals.* Poly (acrylic acid), sodium salt (PAA-Na, Mw= 15,000) were purchased from Polysciences, Inc. Lauric acid (CH\text{3}(\text{CH}_2)_{10}\text{COOH}, ≥98%), palmitic acid (CH\text{3}(\text{CH}_2)_{14}\text{COOH}, ≥99%), stearic acid (CH\text{3}(\text{CH}_2)_{16}\text{COOH}, ≥95%), behenic acid (CH\text{3}(\text{CH}_2)_{20}\text{COOH}, 99%), super hydride solution (1.0M lithium trietlyborohydride in THF) were purchased from Sigma Aldrich.

*ICP analysis.* Standard ICP for iron (TraceCERT, 1000mg/L Fe in nitric acid), multielement standard solution 4 for ICP (TraceCERT, 40mg/L Al, 40mg/L As, 100mg/L B, 40mg/L Ba, 10mg/L Be, 10mg/L Cd, 10mg/L Co, 20mg/L Cr, 20mg/L Cu, 100mg/L Fe, 10mg/L Mn, 20mg/L Ni, 40mg/L Pb, 100mg/L Se, 100mg/L Tl, 40mg/L V, and 100mg/L Zn in 10% nitric acid) were purchased from Sigma Aldrich.

*Commercial iron oxide nanoparticles.* Commercial iron oxide nanoparticles were provided from Advanced Energy Consortium (AEC). Zinc cobalt iron oxide nanopowder/ Nanoparticles (Zn\text{0.5}Co\text{0.5}Fe\text{2}O\text{4}, high purity, 99.995%, 40 nm) and
zinc manganese iron oxide nanopowder/nanoparticles (Zn_{0.5}Mn_{0.5}Fe_{2}O_{4}, high purity, 99.995%, 30-60 nm) were purchased from US Research Nanomaterials Inc. Ferroxide Black 78P was purchased from Rockwood Pigments.

2.2.1.1. Synthesis of iron oxide nanocrystals by thermal decomposition method

The thermal decomposition method involves decomposition of metal precursors in the presence of surfactants in a high boiling point solvent to produce highly monodisperse nanocrystals. One of the unique advantages of this method is nucleation and growth of nanocrystals are produced at different steps.\textsuperscript{76} (Figure 2-1) This makes the formation of monodisperse nanocrystals easier to control. In nucleation, many nuclei are produced at the same time and later these nuclei begin to grow.\textsuperscript{68} The fact that almost all nuclei begin to grow at the same time produces nanocrystals almost identical sizes.
Many researchers have investigated different routes for the synthesis of highly monodisperse nanocrystals. There are many parameters that require modifications to generate monodisperse nanocrystals. In this chapter, I have demonstrated and optimized the conditions of the synthesis of multiple ferrites. Varying sizes of several compositions were obtained from parameter variations, which consequently led to the understanding of the extrinsic properties they may exhibit. The synthetic methodologies utilized for the ferrites are adapted from those previously reported by Colvin\textsuperscript{72} and Hyeon\textsuperscript{73}. 

Figure 2-1. Schematic of thermal decomposition method for the synthesis of monodisperse nanocrystals.
2.2.1.2. Metal oleate synthesis

Metal oleate complexes are formed by the reaction of metal chlorides with sodium oleates.

Iron oleate as an iron precursor was synthesized by the reaction of iron chloride (30 mmol, 8.14g) with sodium oleate (120 mmol, 36.5g) in the mixture of water (75 g) ethanol (60 g), and hexane (98 g) at 60°C for 4 h (Figure 2-2A). The organic phase containing the metal complex product was washed three times with 30 ml of distilled water in a separatory funnel (Figure 2-2B). After the washing process, the solution was further purified with acetone and hexane via centrifugation. 10 ml of the resultant solution was transferred to 50 ml centrifuge tubes and 35 ml of acetone was added. Afterwards, the tube was centrifuged at 11,000 rpm for 15 min (Figure 2-2C). This process was repeated three times and final product (iron oleate complex) was redispersed in hexane and stored in a glass flask (Figure 2-2D).
Figure 2-2. Synthesis steps for metal oleate complex. (A) Experimental setup of metal oleate synthesis (B) metal oleate is washed in separatory funnel with DI water to remove excess salts and by products, (C) metal oleate is purified by centrifugation at 11,000 rpm with 35 mL of acetone and (D) metal oleate is redispersed in hexane and stored in a glass flask at room temperature.

Manganese oleate was prepared by the reaction of manganese chloride tetra hydrate (30 mmol, 5.93 g). Nickel oleate was prepared with nickel chloride hexahydrate (30 mmol, 7.13 g), cobalt oleate was prepared with cobalt chloride hexahydrate (30 mmol, 7.13 g). These oleates were prepared using the same conditions as for iron oleate.
Finally, since zinc oleate could not be synthesized due to the lack of solubility of the complex in organic solvents a combination of iron-zinc oleate was synthesized. For this, iron chloride (30 mmol, 8.10 g) and zinc chloride (15 mmol, 2.09 g) were reacted with sodium oleate (120 mmol, 36.5 g) and in a mixture of water (75 g) ethanol (60 g), and hexane (98 g) at 60 °C for 4 h. For purification, the same steps as for iron oleate were followed.

2.2.1.3. Synthesis of iron oxide nanocrystals

Iron oxide nanocrystals were prepared using iron oleate (from 1 to 10 mmol) as an iron precursor, oleic acid (3 to 30 mmol) as the surfactant, in 10 g of 1-Octadecene (ODE) at 315°C in a 50 ml three-neck round bottom flask equipped with a condenser, magnetic stirrer, thermocouple and heating mantle for 2 h. Figure 2-4 shows a schematic representation of the setup of the synthesis of iron
oxide nanocrystals. The resultant sizes of the obtained nanocrystals with these conditions were from 10 nm to 30 nm.

![Experimental setup of iron oxide nanocrystals synthesis.](image)

**Figure 2-4. Experimental setup of iron oxide nanocrystals synthesis.**

Initially, the reaction was left at 120°C for 1 h to allow for hexane and water evaporation. Then, the temperature was raised to 230°C for 30 min to allow nucleation. Finally, the reaction was further raised to 315°C for 2 h for the growth of nanocrystals.

The parameters that needed to be considered in order to control the size and dispersity of the nanocrystals were reaction temperature, reaction time and the ratio between the iron precursor and the surfactants. All nanocrystals were grown at 315°C for around 2 h. If less time was used, the obtained nanocrystals
exhibited a high polydispersity. In addition to the temperature the ratio between the metal precursor and surfactant was very important for size control. For most iron oxide nanocrystals synthesized, a ratio of 1:3 was used. In order to achieve larger sizes of nanocrystals, modifications in the monomer concentrations were performed. Nanoparticle size follows linearly with monomer concentration; therefore higher monomer concentrations were used to achieve larger monodisperse nanocrystals size. Figure 2-5 shows TEM images of different sizes of iron oxide nanocrystals that were generated from modifying monomer concentration and Figure 2-6 shows the growth of nanocrystals versus the monomer concentrations that were used.

![Figure 2-5. TEM images of iron oxide nanocrystals.](image)

TEM images of iron oxide nanoparticles (A) 10.4 nm, (B) 16.2 nm and (C) 27.4 nm.
Figure 2-6. Growth of iron oxide nanocrystals versus monomer concentration.
Nanocrystals were grown in 10g of ODE. In all reactions, the ratio of Fe-oleate to oleic acid was 1:3.

The resultant nanocrystals were purified using acetone and hexane. 10 ml of the black colloid were transferred to 50 ml centrifuge tubes and 35 ml of acetone were added. This mixture was centrifuged at 4,500 rpm for 25 min. The resultant black precipitate was dispersed in hexane and centrifuged at 4,500 rpm for 25 min. This process was performed three times. The final centrifuge of the nanocrystals dispersed in hexane was performed at 11,000 rpm for 40 min. After this, the nanocrystals dispersed in hexane were stored in a 25 ml vial.
2.2.1.4. Phase transfer of nanocrystals

The synthesized nanocrystals in organic solution were transferred to aqueous solution by using 2-acrylamido-2-methylpropane sulfonic acid-\textit{co}-lauryl acrylate (P[AMPS-\textit{co}-LA]) synthesized in the Colvin Lab.\textsuperscript{63} Phase transfer was successful due to the bilayer formed when the polymer is added to iron oxide nanocrystals solution (Figure 2-7).

\textbf{Figure 2-7. Phase transfer of iron oxide nanoparticles using PAMPS-LA polymer.}
Iron oxide nanocrystals in organic solution were phase transferred using PAMPS-LA by creating a bilayer.

First, the nanocrystal solution in hexane was transferred to diethyl ether. A 1:1 volume ratio of nanocrystal solution to polymer was mixed by magnetic stirring for 2 h keeping the system closed to the external atmosphere. The nanocrystals concentration should be about 100mg/L and polymer concentration around 50mg/L. Then, 5 mL of DI water was added and stirring was continued for one hour. Finally, the system was opened to allow excess solvent evaporation while stirring was continued overnight. The resulting mixture was centrifuged at 4,500
rpm to remove uncoated particles and excess polymer. Then, the solution was centrifuged at 11,000 rpm; resultant precipitate was collected and re-dissolved in DI Water. This was performed twice to produce a solution with no free polymer.

### 2.2.1.5. Surface modification

The surface modification of nanocrystals was performed by using different surfactants with varying length chains. The main focus of investigating the surface modifications was to understand the major factors to prevent aggregation. This is typically dominated by the interparticle interactions which are mainly dictated by the distance between the magnetic cores in a sample. These distances can typically be controlled in solutions by varying the volume percent of the nanoparticles present in solution and in solids by varying the thickness of the surface coating on the particles. Different types of fatty acids to functionalize the surface of the magnetic cores were used; by varying the length of the fatty acid, the distance between the cores both in solution and solid samples would vary. For the synthesis of these samples, instead of using oleic acid as the capping agent the following fatty acids were used: lauric acid (12C), palmitic acid (16C), stearic acid (18C) and behenic acid (22C).

The same thermal decomposition method was used for the synthesis of modified surface nanocrystals. The ratio of metal precursor to surfactant was modified depending on the one used. To obtain further understanding of the process, a mixture of iron oleate (1 mmol), lauric acid (1.5 mmol, 0.300g) in 10 g of ODE was heated to 315°C for 2 h. For nanocrystals modified with palmitic acid as
surfactant, the ratio between iron precursor and palmitic acid was 1:2. For stearic acid, the ratio used was 1:2. Finally, the ratio for iron precursor to behenic acid was 1:1.5. Figure 2-8 shows TEM images of the resultant iron oxide nanocrystals generated by the modification of the surface with different capping agents.

Figure 2-8. TEM images of iron oxide nanocrystals capped with different surfactants.
TEM images of iron oxide nanocrystals with modified capping agents. (A) Lauric acid, (B) palmitic acid, (C) stearic acid and (D) behenic acid.

2.2.2. Coprecipitation synthesis of iron oxide nanocrystals

To avoid the intensive nature of water transfer work to obtain water soluble nanocrystals, a coprecipitation method was utilized. Coprecipitation is a convenient
method to synthesize water-soluble nanocrystals from iron salts solution and an alkaline hydroxide source under an inert atmosphere at room temperature (Figure 2-9). \(^\text{77,78}\)

![Figure 2-9. Schematic of coprecipitation synthesis of iron oxide nanoparticles.](image)

Metal salts are stirred for 30 min. Then, metal salt solution is injected drop by drop into a 1M NaOH solution previously heated to 90°C.

A mixture of iron (II) chloride (0.1M, 1.0g) and iron (III) chloride (0.2M, 2.7g) in 50 mL of DI water was prepared in a 100 mL three neck flask. The solutions were stirred and purged with \(\text{N}_2\) for 30 min. Then, the solution was transferred to a 60 mL syringe and slowly injected to a 1 M NaOH solution which was heated to 90°C. After completing the iron salt addition process, the reaction was kept stirring for 30 min at 90°C. When the reaction was completed and cooled down, the solution was transferred to a 50 mL centrifuge tube. The nanoparticles were washed several times with DI water until the pH of the solution reached 7. Finally, the resultant nanoparticles were dried in a desiccator overnight.
2.2.3. Solvothermal synthesis

Another method of nanoparticle synthesis utilized was the solvothermal synthesis. The synthesis of iron oxide nanoparticles was carried out in a Teflon-lines stainless steel autoclave (50 mL). Metal salts (FeCl₃, ZnCl₂, MnCl₂, NiCl₂, CoCl₂), capping agent (PVP, PEG, PVA and citrate) and solvents (ethylene glycol, diethylene glycol or their mixture) were all mixed in a beaker and stirred at 400 rpm at room temperature for 30 min or until solution was completely homogenous (Figure 2-10A). The mixture was transferred to the Teflon liner and placed into the stainless steel autoclave (Figure 2-10B). The autoclave reactor was well sealed and placed in an oven previously heated at 200°C. The reaction was left at 200°C for 24 h. After the reaction was completed, the mixture was cooled down at room temperature and transferred to a 25 mL vial (Figure 2-10C). The product was washed three times with ethanol and water to remove unreacted reactants and byproducts. The product was collected using a cubic magnet (Figure 2-10D). Finally, the samples were dried in an oven at 80°C overnight.
Figure 2-10. Experimental setup for solvothermal synthesis.
(A) Metal salts, solvent and capping agents are stirred at room temperature, (B) mixture is places in an autoclave and it is places in an oven at high temperature, (C) mixture after the reaction has been completed and (D) highly magnetic nanoparticles are collected with a magnet.

2.3. Purification setup

Purification is one of the most crucial steps after the nanoparticles have been synthesized. Centrifugation is a process that is used for particle mixture separation, consisting of different densities and masses in a liquid. It is already well known technique is used for protein purification in biochemistry and has become an ideal method to purify the synthesized nanocrystals and remove all unreacted products from the final nanocrystal solution. Typically, two different types of centrifugation are used: low speed centrifugation and high-speed centrifugation. The type of centrifugation chosen depends on the nanocrystals being purified.
2.3.1. Low speed centrifugation

Thermo Scientific Multifuge 1SR Refrigerated Benchtop Centrifuge was used for standard purification of nanocrystals. The centrifuge was used to separate nanocrystals from unreacted species. The lower speeds used were 4,500 rpm (rotation per minute) and 11,000 rpm. Pairs of centrifuge tubes were balanced within 0.1 g with respect to one another. This type of centrifugation was typically used when purifying nanocrystals in organic media.

2.3.2. Ultra high speed centrifugation

Beckman- Coulter Optima L-80 XP Ultracentrifuge was used for ultra high speed centrifugation. This ultracentrifuge was used to force separation of nanocrystals already in solution, specifically when purifying nanocrystals after phase-transfer process. The rotors that were used were where 45Ti which used specialized vials (Beckman Polycarbonate Centrifuge Bottles with caps) of 50 ml and rotor 70Ti which used vials of 25 ml. Vials were balanced in pairs within a 0.05 g sensitivity with respect to one another. Samples were run at 35,000 rpm for 1 h at 10°C. This process was performed three times or until the supernatant appeared to be was completely (visually) clear. This type of centrifugation was used when phase-transfer was performed to the nanoparticle since higher speeds are required to get nanoparticles out of solution.
2.4. Instrumentation

2.4.1. Physicochemical characterization

2.4.1.1. Transmission Electron Mircoscopy (TEM)

The nanocrystal sizes were measured using a transmission electron microscope. Samples were prepared by adding droplets (20-30 μL) of diluted solution to an ultra thin type-A 400 mesh copper grid from Ted Pella Inc. and were left to dry under air. TEM micrographs were taken by a JEOL 2100 Field Emission Gun TEM operating at 200 kV with a single tilt holder. Size and size distribution were obtained from counting more than 1000 nanoparticles using Image Pro or Image J software.

2.4.1.2. Scanning Electron Microscopy (SEM)

SEM images were taken on an FEI Quanta 400F Field Emission Scope at 10.0 kV. Samples were placed in SEM mounts using carbon tape.

2.4.1.3. X-Ray Diffraction (XRD)

X-ray diffraction patterns of the samples were collected using a Rigaku D/Max Ultima II. 2θ range was from 10 to 80 degree with a Cu Kα radiation (1.54 Å) and the X-ray was generated at 40 kV and 40 mA. Liquid samples were
deposited on glass substrates from their hexane dispersions until the substrate was completely covered by the solution. Powder samples were analyzed using a 5 mm diameter x 0.2 mm deep Rigaku zero-background sample holder. Sample used for analysis was ~100 mg of powder. Jade 10.0 software was used to match expected ferrite peaks.

2.4.1.4. X-Ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy data was collected using PHI Quantera XPS in a aluminium foil substrate with an X-ray spot size of 200.00 μm with pass energy of 26.00 eV at 45.0°. Time of analysis varied depending on the composition. PHI Multipak 7.0 software was used to process the data.

2.4.1.5. Dynamic Light Scattering (DLS)

Dynamic light scattering analysis was performed using a Zetasizer NanoZS from Malvern Company. Zetasizer NanoZS uses a He-Ne laser 633 nm and temperature range from 25 to 90°C. Refractive index for magnetite used was 2.42. Typically triplicates were obtained for each sample. The instrument automatically optimized the analysis for the number of scans per measurement. For high temperature measurements quartz cuvettes were used.
2.4.1.6. Thermal Gravimetric Analysis (TGA)

Thermo-gravimetric analysis was performed on a Q-600 Simultaneous TGA/DSC. A 6 x 2.5 mm diameter alumina pan was used as sample holder. For analysis, temperature was maintained at 35°C for 10 minutes for instrument stabilization. Later, samples were heated to 800°C at a rate of 10°C/min under argon.

2.4.1.7. Brunauer- Emmet Tellet (BET) surface area analysis

Multipoint BET surface area was collected in a Quantachrome Autosorb-3B. Degassing was performed by heating the samples to 200 °C for 3 h. Surface area was calculated automatically using an Autosorb-3 software.

2.4.1.8. Inductively Coupled Plasma-Emission Optical Spectroscopy

All samples were analyzed by Natalia I. Gonzalez-Pech. The nanoparticle concentrations were measured by a Perkin Elmer Optima 8300 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) equipped with an autosampler. All measurements were carried out with calibrations R> 0.999 and LOQ lower than 0.2mg/L. Each metal was measured in two wavelengths. For iron 273.955 nm and 238.204 nm, manganese 294.93 nm and 257.61 nm, zinc 206.30 nm and 213.85 nm, cobalt 228.61 nm and 231.16 nm and nickel 231.60 nm and
234.47 nm were used respectively. Calibration curves had standards between 1-60mg/L.

Sample digestion was performed by adding 1mL of HNO₃ trace metals to 20-50μL of sample solutions. The sample was heated and stirred in a hot plate for 2h or until solution turned completely clear. The solution was transferred to a 10mL volumetric flask and diluted to 10mL using deionized water. The solution was filtered with a 0.2μm PES syringe and transferred to 15mL centrifuge tube.

2.4.2. Magnetic characterization

2.4.2.1. Super Quantum Interference Device (SQUID)

Magnetic studies were carried out using a MPMS Quantum Design magnetometer (Figure 2-11). Measurements performed on this Super quantum interference device (SQUID) were carried out with fields up to 7 T and temperatures from 5 to 400 K. An applied field was employed to evaluate parameters such as magnetic susceptibility ($\chi_v$), magnetic saturation ($M_s$) and coercivity ($H_c$) of the synthesized materials. Magnetic susceptibility was measured at low fields, from 0-50 Oe in 5 Oe steps in order to simulate fields which will be applied in any contrast agent applications and can be calculated using Equation 2-1.

$$\chi_v = \frac{M}{H}$$

Equation 2-1. Magnetic susceptibility
Magnetic susceptibility was typically measured at two temperatures: room temperature as well as high temperatures (373K and 423K). High temperatures were used to simulate the reservoir environment to observe any adverse effects. Additionally, the magnetic response to an applied magnetic field was measured from -5 Teslas (T) to +5 T. These were performed in order to observe the magnetic response of the materials as well as to investigate the presence of magnetic coercivity. More over, measurements such as Zero Field Cooled- Field Cooled (ZFC-FC) were performed to look at the blocking temperature of each sample, $T_B$. For this sequence, the samples is first cooled from room temperature (298K) to 5K without any applied field. Later, a weak field is applied from cooling temperatures to room temperature and differences are observed which relate directly to the blocking temperature if the material exhibits latent magnetization. An advantage to magnetic measurements using SQUID are that samples could be solids, liquids and films.
For liquids, a 5mm High Grade NMR sample tube was used to hold the sample. The sample was added using a 1 ml syringe with a long metallic needle. After the sample was added the tube was sealed under vacuum with a butane torch to prevent evaporation of the sample since it is crucial to know the exact mass that is being analyzed. The NMR sample tube was mounted into a straw, which was later mounted in the SQUID for analysis.
**Figure 2-12. Liquid sample preparation for magnetic analysis.**
(A) Sample transferred into the NMR tube, (B) NMR is sealed under vacuum using a butane torch and (C) sample is mounted in the SQUID's rod.

For solids, powders were tightly packed in saran wrap. A small piece of saran wrap was weighed. Then, the powder of interest was added and mass was recorded. The powder was then tightly packed in the saran wrap and further mounted into the straw for analysis.
Figure 2-13. Sample preparation of powder sample analysis in SQUID. (A) piece of saran wrap is weighed, (B) powder sample is added to the saran wrap, (C) powder is tightly packed and (D) sample is loaded in a stra for analysis.

2.4.2.2. Vibrating Sample Magnetometer (VSM)

*Instrument located in UT Austin.* Magnetic studies were performed in a EV7 Vibrating Sample Magnetometer (Figure 2-14) from Microsense at room temperature. An applied field was employed to evaluate parameters such as magnetic susceptibility ($\chi_v$), magnetic saturation ($M_s$) and coercivity ($H_c$) of the synthesized materials. Magnetic susceptibility was measured at low fields, from -3 to 3 Oe in 0.040 Oe steps. Magnetic susceptibility was typically measured at 300K. Magnetic saturation values were obtained from hysteresis curve at room temperature. Samples were magnetized in 200 Oe steps until 1 T. Then, field was applied in opposite direction from 1 T to -1 T in 200 Oe steps to observe possible coercivity or remanescence.
A 6 mm acrylic case with lid was used for both solid and liquid samples. A known volume was added to the cups for magnetic analysis.

Figure 2-15. Sample preparation for liquid samples in VSM. (A) Acrylic VSM cup holders, (B) addition of known volume of sample and (C) acrylic cup is sealed with a lid.
Chapter 3

Commercial iron oxides nanoparticles for downhole imaging

3.1. Introduction

Currently, there has been a growing interest in utilizing nanotechnology into the oil and gas industry. Nanomaterials offer intrinsic characteristics applicable towards the major problems this industry is facing. The Advanced Energy Consortium (AEC) a group of academic and industrial researchers formed for the betterment of oil and gas production, have as their main function, the development of micro and nanotechnologies for the oil and gas industry. A key are of challenge in the oil and gas industry is to be able to obtain accurate information on the geological substructure. Nanoparticles have been hypothesized as serving as contrast agents, akin to MRI contrast agents to help identify the fine details of the reservoirs.
Nanocrystals have unique physical and chemical properties such as high surface areas and uniform sizes and magnetic properties that not even their bulk counterpart are not able to achieve.\textsuperscript{79,80} With the small size capable of penetrating formations, and wealth of magnetic properties, there is an increase of potential to target desired applications due to the control at the atomic level. For example, ferrites due to their size and composition show high initial susceptibilities hence possess no coercivity. These characteristics are ideal for imaging applications because superparamagnetic materials tend to have a rapid response when a magnetic field is applied. This chapter centers on determining the relationship between the characteristics of the nanoparticles (size, surface coating, composition, etc.) and the magnetic susceptibility of the materials. In addition, the commercial nanoparticles were also studied in similar conditions found in conventional reservoirs, where there would be high temperatures, high pressures and salinities. This study would help to define the requirements for a material to serve as a nanomagnetic contrast agent for down-hole applications.

\section*{3.2. Materials characterization}

For comparative purposes, the AEC provided several commercial iron oxide nanoparticle samples in solution. Seven samples of ion oxides were supplied: A, B, C, D, I, L and K. Samples A, C, D and L were dispersed in water while B, I and K were dispersed in kerosene. TEM was used to obtain the size and size distribution
Commercial nanoparticles range in size from 4 to 12 nm and typically showed a 40% polydispersity.

**Figure 3-1. TEM of commercial iron oxide nanoparticles.**

TEM images of commercial iron oxide colloids (A) Sample A, (B) Sample B, (C) Sample C, (D) Sample D, (E) Sample I, (F) Sample K and (G) Sample L.

Sample A was the smallest (4.8 nm) while the others had a similar size (around 10 nm). For sample L, it was not possible to perform a size analysis due to the extensive aggregation. In addition, dynamic light scattering (DLS) was performed to analyze the hydrodynamic diameter of the iron oxide nanoparticles at room temperature (Table 3-1). From DLS measurements, it was observed that all samples dispersed in water (A, C, D and L) were functionalized with a large capping agent while the dispersed in kerosene (B, I, and K) a small capping agent was used.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>DLS at 25° (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>Water</td>
<td>27.5 ± 1.50</td>
</tr>
<tr>
<td>Sample B</td>
<td>kerosene</td>
<td>11.2 ± 0.64</td>
</tr>
<tr>
<td>Sample C</td>
<td>Water</td>
<td>33.5 ± 3.21</td>
</tr>
<tr>
<td>Sample D</td>
<td>Water</td>
<td>41.1 ± 1.39</td>
</tr>
<tr>
<td>Sample I</td>
<td>kerosene</td>
<td>13.7 ± 0.29</td>
</tr>
<tr>
<td>Sample K</td>
<td>kerosene</td>
<td>13.4 ± 0.62</td>
</tr>
<tr>
<td>Sample L</td>
<td>Water</td>
<td>20.2 ± 0.16</td>
</tr>
</tbody>
</table>

**Table 3-1. Hydrodynamic diameter analysis at 25°C of commercial iron oxides.**

Table summarizes the hydrodynamic diameter measured in DLS for commercial iron oxide nanoparticles dispersed in water and oil based solvent.

Furthermore, XRD profiles were performed for the commercial iron oxide samples with iron oxide reference peaks in red (Figure 3-2). XRD was used to verify the crystallinity of the samples in both solvents. All observed peaks agree with magnetite patterns show in red. Although with XRD it was not possible to confirm if the iron oxide species present are magnetite or maghemite.
Figure 3-2. XRD patterns of commercial iron oxide samples.
XRD patterns of commercial iron oxide samples in solution. Red lines correspond to the expected peak positions and intensities for magnetite (JCPDS #190629).

In addition, commercial ferrite powder samples were also characterized. Magnetite (P78) was purchased from Rockwood Pigments. Manganese zinc ferrite and cobalt zinc ferrite were bought from US Research Nanomaterials Inc. These powder samples were also characterized with TEM for size and size distribution. From the TEM of commercial magnetite (Figure 3-3A) it was observed that the material was made of aggregates of particles of around 100 nm. Figure 3-3B, shows TEM image of manganese zinc ferrite nanopowder where particle aggregates of around 20-50 nm were observed. Finally, Figure 3-3C shows TEM image of cobalt zinc ferrite nanoparticles which shows aggregated nanoparticles of around 40 nm. It can be observed that they are aggregated.
Figure 3-3. TEM images of commercial nanopowders.
TEM images for commercial ferrite powders (A) Fe₃O₄, (B) MnZnFe₂O₄ and (C) CoZnFe₂O₄.

Further investigation of commercial magnetite by XRD confirms that crystalline magnetite is present in the commercial samples (Figure 3-4).
Figure 3-4. XRD patterns of commercial ferrite nanocrystals.
XRD diffractograms for commercial nanopowders. Red lines correspond to the expected peak positions and intensities for magnetite (JCPDS #190629).

3.3. Effect on environmental conditions on magnetic behavior

The main objective of this study was a complete magnetic characterization of all magnetic nanoparticles available for use as contrast agents. There are several key parameters needed for a useful contrast agent: 1) a high initial susceptibility at low fields, and 2) magnetic nanoparticles should develop a superparamagnetic behavior (no coercivity in the hysteresis at 300K). The main property that was considered in this section was the effect that concentration and temperature have on the magnetic properties.
First static and dynamic studies were performed to investigate the reproducibility of SQUID measurements. Sample A was chosen as the model sample. For static analysis, the same sample was measured in triplicates. Whereas, in dynamic analysis the samples were prepared three times and each was analyzed. Sample preparation is described in Chapter 2. Figure 3-5A shows the static analysis of sample A at a concentration of 0.5% by volume. It can be observed that there is no significance change in the magnetic susceptibility (slope of the curve) of the sample. Figure 3-5B shows the dynamic analysis of the same sample (Sample A at 0.5 v%) and it can be seen that there is a small change in the value of magnetic susceptibility but still not very significant. From this data, we can conclude that the use of the SQUID magnetometer can provide reproducible magnetic data.

![Figure 3-5](image)

**Figure 3-5. Reproducibility of magnetic measurements in SQUID.**
(A) Static analysis and (B) dynamic analysis for sample A at a concentration of 0.5% by volume.
The stock solution of sample A (4.3 v%) was analyzed in the same manner. The static analysis shown in Figure 3-6A, the same sample was analyzed three times and found no significant effect on the initial susceptibility. On the other hand, Figure 3-6B shows the dynamic repeatability study for sample A, where three different samples were prepared and analyzed in SQUID and greater variability of the initial susceptibility values was observed. This increased variability is most likely coming from an error from the mass determination during sample preparation.

**Figure 3-6. Reproducibility of magnetic measurements in SQUID.**
(A) Static analysis and (B) dynamic analysis for sample A at a concentration of 4.3 v%.

### 3.3.1. Concentration effect

Magnetic characterization was performed from 0 to 50 Oe (0-4000A/m SI in units) at different concentrations (0.5 v/v%, 1.0 v/v%, 1.5 v/v%, 2.5 v/v% and 5.0 v/v%) using a SQUID magnetometer. Figure 3-7 shows the room temperature
magnetization data for sample A. It can be observed an increase in the initial susceptibility (slope of the curve) as the concentration increases.

![Diagram showing concentration dependence of sample A.](image)

**Figure 3-7. Concentration dependence of sample A.**
Magnetization versus applied field of five different concentrations of Sample A.

The same magnetization data was collected for all commercial iron oxide samples. From all samples provided, most promising iron oxides (A, C, I and K) were chosen for a comparison against each other. These samples were dispersed in water (A and C) and in kerosene (I and K). A linear relationship from the magnetic susceptibility and the concentration (volume percent) of each sample was plotted (Figure 3-8). It can be observed that for all four samples as the concentration increases there is an increase in the magnetic susceptibility. This relationship helped to predict the concentration needed of the materials for a desired magnetic
susceptibility. Even though all samples are considered to have similar composition, and size, as described above, each sample has a unique rate of increment in the magnetic susceptibility as a function of concentration. If one only considers this rate as a factor to determine the best candidate for field trial, sample C would be the ideal one. However, this factor is not the only consideration to take into account; the stability at high temperatures and the cost of the material are also critical when choosing the best commercial material for field trial.

![Figure 3-8. Linear relationship between magnetic susceptibility and concentration (volume percent).](image)

3.3.2. Temperature effect

The conventional reservoir environment in regards to temperature is 75-125°C. Therefore, magnetic characterization was performed at two temperatures
(300K and 350K) for all samples. Figure 3-9 shows magnetization data for Sample A at both temperatures for three different concentrations. It can be observed that there is not a significant change in the magnetic susceptibility of the sample. This is encouraging in that if there was a dramatic loss of magnetization as temperature increases, the materials would not be good candidates for reservoir measurements.

![Graph showing magnetization data for Sample A at 300K and 350K](image)

**Figure 3-9. Temperature effect on magnetization of commercial sample A.** Magnetization versus applied field of three different concentrations of sample A at (A) 300K and (B) 350K.

In addition, samples that were dispersed in kerosene were analyzed at even higher temperatures since the solvent had a higher boiling point. A conventional SQUID could only go up to 400K. Therefore, a high temperature furnace (Figure 3-10A) was installed in the SQUID. The furnace has a capability of running from 300K to 800K, which was able to measure the magnetic behavior at high temperatures to model hotter reservoirs. Sample preparation was similar to the
one used for liquid samples (described in Chapter 2) but the sample holder was a melting point tube instead of an NMR tube. The melting point tube was inserted into the brass sample holder (Figure 3-10B) for analysis. Figure 3-10C shows magnetization data of Sample I at three different temperatures (300K, 350K and 423K). It is observed that there is no drastic change in the magnetic susceptibility even when we go much higher in temperature.

![Figure 3-10](image.png)

**Figure 3-10. Magnetic data at high temperature.**
(A) SQUID oven, (B) brass sample holder and (C) magnetization versus applied field of sample I at 300K, 350K and 423K.

Table 3-2 summarizes all magnetic susceptibility values in SI units collected for all commercial samples of iron oxide provided from AEC at different concentrations and temperatures.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Concentration (v/v%)</th>
<th>Magnetic susceptibility ($\chi_v$) at 300K</th>
<th>Magnetic susceptibility at ($\chi_v$) 350K</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.5</td>
<td>0.15</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.25</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>0.28</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>0.58</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>4.3</td>
<td>0.87</td>
<td>0.73</td>
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<td>0.21</td>
<td>0.19</td>
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<tr>
<td></td>
<td>1.0</td>
<td>0.36</td>
<td>0.32</td>
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<tr>
<td>C</td>
<td>1.5</td>
<td>0.96</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>1.60</td>
<td>1.34</td>
</tr>
<tr>
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<td>4.9</td>
<td>1.76</td>
<td>1.56</td>
</tr>
<tr>
<td>D</td>
<td>0.5</td>
<td>0.22</td>
<td>0.17</td>
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<tr>
<td></td>
<td>1.0</td>
<td>0.27</td>
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<td></td>
<td>6.6</td>
<td>2.03</td>
<td>1.73</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.09</td>
<td>0.07</td>
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<tr>
<td>L</td>
<td>1.0</td>
<td>0.16</td>
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<td>8.0</td>
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<td>0.11</td>
</tr>
<tr>
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<td>1.0</td>
<td>0.16</td>
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<tr>
<td></td>
<td>1.5</td>
<td>0.54</td>
<td>0.41</td>
</tr>
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</table>
### Table 3-2. Summary of magnetic data collected for the commercial iron oxide samples.

Table summarizes magnetic susceptibilities at different volume percent concentration at 300K and 350K.

#### 3.4. Effect on environmental conditions in stability

One of the major challenges that nanoparticles would face is the harsh conditions that would be present in an oil reservoir such as high temperatures and high salinities. Therefore, stability studies were performed for the commercial nanoparticles under similar conditions found in a reservoir.
3.4.1. Temperature effect

Long term stability at 90°C of commercial samples A, C, I and K at a concentration of 0.5% by volume was monitored over a three month period. Every week a portion of each of the samples were diluted to 1% by weight and were analyzed using dynamic light scattering (DLS) to look at the change in the hydrodynamic diameter after being stored in a sample oven at 90°C. Initial visual evaluation was also performed to determine if large precipitates were present. The DLS measurement was performed at 90°C to prevent a temperature shock, which could alter the results. During the first week the particles hydrodynamic diameter started to decrease possibly due to a disaggregation of the material. As time progressed, the size started to increases likely due to an excess of kinetic energy in the system causing aggregation. As shown by the large size increase at week 3, sample C was completely aggregated (Figure 3-11). Therefore, no further studies on that sample could be conducted. After the fourth week, aggregation started to occur for samples I and K. From the data, it was observed that sample A was the most stable material at elevated temperature conditions. The initial hydrodynamic diameter for sample A was 77 nm and the final size measured at the end of the study was 84 nm. (Figure 3-11A and Figure 3-11B).
3.4.2. Salinity effect

Salinity is a factor that needs to be considered for nanoparticles since they will be injected into the reservoirs. The conventional reservoir environment in regards to salinity is 50,000 ppm- 150,000 ppm (max-300,000 ppm as NaCl). Salinity studies were needed to determine nanoparticles stability under similar conditions as reservoirs.

Sample A was chosen as the model sample to perform stability tests at 25°C in the water injection fluids (provided from AEC).

The test shows that after 6 h of being suspended in the injection fluids the materials start aggregating. Sample A in water injection fluid (W83) seems to be a
little more stable than in water injection fluid (W1440) (Figure 3-12). After 48 h, the material is completely aggregated in both injection fluids as indicated by the large increase of the hydrodynamic diameter of the commercial nanoparticles (Table 3-3). Also, from the pictures of the solutions it can be clearly observed the aggregation of the sample.

**Figure 3-12. Sample A in water injection fluids.**
After 6 hours (A) Sample A in injection fluid W84 and (B) Sample A in injection fluid 1440. After 48 h (C) sample A in injection fluid W84 and (D) sample A in injection fluid W 1440.
Table 3-3. Stability study with DLS of commercial sample A in injection fluids.
Table summarizes the hydrodynamic diameter of sample A in water injection fluids at several time periods.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Size of sample A Water Inj. 84 (nm)</th>
<th>Size of sample A Water Inj. 1440 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>33.9</td>
<td>33.6</td>
</tr>
<tr>
<td>1</td>
<td>51.9</td>
<td>34.3</td>
</tr>
<tr>
<td>6</td>
<td>70.5</td>
<td>88.0</td>
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<tr>
<td>8</td>
<td>77.9</td>
<td>114</td>
</tr>
<tr>
<td>12</td>
<td>189.3</td>
<td>342.5</td>
</tr>
<tr>
<td>48</td>
<td>288.2</td>
<td>1346</td>
</tr>
</tbody>
</table>

In addition to stability studies on the particle aggregation in brine, magnetic analysis was performed for sample A in water injection fluids. Sample A was analyzed in water injection fluid W84 at a concentration of 0.5% by volume in triplicates. The fluid was chosen because nanoparticles had greater stability that the water injection fluid W1440 from DLS study. Figure 3-13A shows the initial magnetic susceptibility data for sample A in water; whereas Figure 3-13B shows susceptibility data for sample A dispersed in water injection fluid W84 at the same concentration. From the data, it was observed that there is a significant decrease in the magnetic response when the nanoparticles are dispersed in the injection fluid. This could possible be due to the excess of salts and impurities present in the fluids, which could be reacting with the surfactant present in the nanoparticle. Thus, causing aggregation of nanoparticles and affecting their magnetic performance.
Figure 3-13. Magnetic data of sample A in injection fluids. Magnetization versus applied field of (A) sample A and (B) sample A in water injection fluid W84. Concentration of sample analyzed was 0.5\%.

3.5. Conclusions

For nanoparticle systems to be utilized as effect contrast agents, they must withstand reservoir conditions and keep their magnetic properties. For the commercial samples, all nanomaterials that were studied had a polydispersity of around 40\% which will give rise to unpredictable results over time. Lastly, from the magnetic data obtained for each commercial nanoparticle at different concentrations it was observed that susceptibility increased as concentration of the material increased. A linear relationship was found between these two parameters. This would help to predict the concentration of nanomaterial for an ideal magnetic susceptibility.
Commercial nanoparticles were tested in similar conditions as a conventional reservoir. It is crucial that these nanoparticles survive under the harsh conditions present in a reservoir such as high temperatures, high salinities and high pressures. First, a stability study was performed for the nanoparticles. These were stored in an oven at 90°C and analyzed every week in DLS for a period of 3 months. The most stable sample at high temperatures was sample A. In addition, magnetic data was collected at high temperatures to observe any significant change in the magnetic response. Data showed that although there is a drop in the magnetic susceptibility, it is not very significant which makes them promising nanomaterials. Finally, nanoparticles were tested in similar salinity conditions. For this study, water injection fluids were provided from AEC. These were typical in produced water injection fluids used in water-flooding which contain large salt concentrations and other impurities that are present down-hole. Commercial nanoparticles showed aggregation after only several hours in these injection fluids.

The initial results on commercial samples were useful to obtain in understanding of the current technology and what areas need to be improved to function as suitable contrast agents for down hole imaging. While the magnetic properties were stable at temperature, there is a severe polydispersity issue coupled with a lack of stability in salt conditions. To overcome these challenges a focused approach to create specific nanoparticle systems, with enhanced magnetic properties and stability is necessary to obtain materials which meet all requirements for reservoir imaging.
Chapter 4

Synthesis of magnetic multi-metal nanocrystals

4.1. Introduction

Magnetic properties of nanomaterials such as susceptibility and saturation magnetization are strictly governed by their size, composition and crystallinity. Size of nanoparticles is a vital parameter to consider due to the effect it has on the magnetic properties of nanomaterials. As discussed in Chapter 1, when particles decrease in size, they go from exhibiting bulk magnetic effects in a multidomain regime, to a point where there is only a single domain present. At a certain point in size, the material will no longer be able to exhibit the properties of a single domain. When material exhibits a strong magnetic moment but no longer exhibits remnant magnetization at zero field, i.e. no coercivity, it is known as the superparamagnetic regime. These small magnetic nanoparticles become rapidly
magnetized when an external field is applied.\textsuperscript{16} For use as contrast agents, the nanomaterials need to be in the superparamagnetic regime since they exhibit a greater sensitivity to magnetic fields and possess no coercivity which would actually cause a worsening of the imaging. This rapid response to applied field and immediate return to a non magnetic resting state are the ideal qualities to maximize imaging capability.

In addition to size composition plays a critical role on the magnetic properties of nanocrystals.\textsuperscript{84} Spinel ferrites MFe$_2$O$_4$ (M= Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$) offer expanded magnetic properties because of the implementation of other transition metals ions rather than Fe$^{2+}$ ions, which can have more unpaired electrons, therefore altering their magnetic response.\textsuperscript{85,86} Spinel ferrites are classified as normal, inverse and mixed spinels. In normal spinels, divalent ions occupy tetrahedral sites and trivalent ions occupy octahedral sites. In an inverse spinel, divalent ions occupy half of the octahedral sites and trivalent ions are distributed in tetrahedral and octahedral sites. Lastly, in a mixed spinel divalent and trivalent ions are distributed in both tetrahedral and octahedral sites. Magnetic properties of spinel ferrites are strictly linked to the distribution of cations between the tetrahedral and octahedral sites. The distribution control of metal ions provides a means to customize the properties of spinel ferrites.\textsuperscript{87} Spinel ferrites are known to be soft magnets which means that materials reach saturation at low fields and have high initial magnetic susceptibilities and low coercivities. The synthesis and characterization of varied ferrites and their magnetic properties will be discussed in this chapter.
4.2. Synthesis of iron oxide nanocrystals

4.2.1. Iron oxide nanocrystals synthesis through non-hydrolytic route

The synthesis of the iron oxide nanoparticles is a two-step process as previously discussed in Chapter 2. The first step involves the synthesis and purification of the metal precursor, a metal oleate complex. The second step encompasses the growth of the nanoparticles by thermal decomposition of the metal precursor. The synthesis of magnetite consists of a mixture of 1 mmol of iron oleate dissolved in 10 g of 1-Octadecene and 3 mmol of oleic acid in a 50 mL round flask. First, the mixture is heated at 120°C for 1 h to let water and hexane evaporate. The temperature is then increased to 230°C for 30 min, leading to the initiation of nucleation of the nanocrystals. Finally, for the growth stage the mixture is heated to 320°C for 1 h.

![TEM images of iron oxide nanocrystals](image)

**Figure 4-1. TEM images of iron oxide nanocrystals.**
TEM images of magnetite nanocrystals (A) 10.4 nm, (B) 16.2 nm and (C) 27.4 nm.

The concentration of the iron precursor and the ratio between iron precursor and surfactants are important parameters to control the diameter of
monodisperse nanocrystals. Increasing the concentration of the iron precursor from 1 mmol to 10 mmol in a fixed amount of ODE grew larger nanocrystals; nanocrystals which ranged from 10 to 27 nm (Figure 4-1). Iron oleate complex was used as an iron precursor with oleic acid as the surfactant and the ratio of iron oleate to oleic acid was fixed to 1:3.

4.2.2. Nanocrystals via coprecipitation method

Iron oxide nanoparticles synthesized by coprecipitation method were prepared by the mixture of 0.1 M FeCl$_2$ (1.0g), 0.2 M FeCl$_3$ (2.70g) and 50mL of DI water in a 100 mL round bottom flask. The mixture was purged with pure N$_2$ for 5 to 10 min followed by 30 min of mixing. The metal salt solution was then transferred dropwise via syringe to a separate round bottom flask, which contained 200 mL of 1 M NaOH that was heated to 90°C, purged with N$_2$ and vigorously stirred for 30 min. Manganese ferrite and zinc ferrites were also synthesized via this method substituting 0.1 M MnCl$_2$ (0.99g) and 0.1M ZnCl$_2$ (0.68g) (instead of 0.1 M FeCl$_2$) for manganese and zinc ferrite, respectively instead of 0.1M FeCl$_2$. Figure 4-2 shows TEM images of the ferrite nanocrystals synthesized clearly demonstrating that large aggregates are observed for all compositions. These optical observations demonstrate that this synthetic route is not the ideal as it leads to the high polydispersity of nanoparticles which will result in uncertain and irreproducible properties over time.
Figure 4-2. TEM images of ferrite nanocrystals synthesized through coprecipitation.

TEM images of ferrite nanocrystals via coprecipitation (A) Fe₃O₄, (B) MnFe₂O₄ and (C) ZnFe₂O₄.

X-ray powder diffraction was performed to characterize crystallinity and structural determination for the synthesized ferrite nanocrystals via coprecipitation method. Data shows XRD spectra for Fe₃O₄ and MnFe₂O₄ match with the expected peaks of hematite and zinc ferrite spectrum matches with expected peaks of magnetite (Figure 4-3). Magnetite reference is used for ferrites since they have the same crystalline structure.
4.3. Synthesis and characterization of ferrite nanocrystals

One of the advantages of ferrites is that their compositions can be greatly varied which leads to an ideal optimization of their properties. As previously discussed in Chapter 1, spinel ferrite structures such as Fe$_3$O$_4$, CoFe$_2$O$_4$, MnFe$_2$O$_4$ and NiFe$_2$O$_4$ exhibit large magnetization values since the substitution of Fe$^{2+}$ for other metals enhances the interactions between the A and B sites. For example, the addition of Zn$^{2+}$ ions, which prefer octahedral sites, creates a
disproportion between the Fe$^{3+}$ ions in both tetrahedral and octahedral sites leading to an increase in the magnetic moment. Therefore, synthesis and magnetic properties of bimetallic ferrite will be discussed to understand their magnetic behavior and potential applications.

4.3.1. Bimetallic ferrite nanocrystals

Manganese iron, nickel iron, cobalt iron and zinc iron ferrites were prepared as described below via non-hydrolytic route which led to discrete nanoparticles with narrow polydispersity.

4.3.1.1. Synthesis of manganese iron oxide ($\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$)

The mixture of iron oleate (1 mmol) and manganese oleate (0.5 mmol) were reacted with 3 mmol of oleic acid in 10 g of 1-octadecene (ODE) at 315°C for 2h.

4.3.1.2. Synthesis of nickel iron oxide ($\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$)

The mixture of iron oleate (1 mmol) and nickel oleate (0.5 mmol) were used reacted 3 mmol of oleic acid in 10 g of 1-octadecene (ODE) at 315°C for 2 h.

4.3.1.3. Synthesis of cobalt iron oxide ($\text{Co}_x\text{Fe}_{3-x}\text{O}_4$)

The mixture of iron oleate (1 mmol) and cobalt oleate (0.5 mmol) were used reacted 3 mmol of oleic acid in 15 g of 1-octadecene (ODE) at 315°C for 2 h.
4.3.1.4. Synthesis of zinc iron oxide (Zn$_x$Fe$_{3-x}$O$_4$)

The mixture of iron-zinc oleate complex (1 mmol) were reacted with 3 mmol of oleic acid in 10 g of 1-octadecene 315°C for 2 h.

4.3.1.5. Bimetallic nanocrystal characterization

The bimetallic ferrites were characterized with TEM for size and size distribution, XRD to confirm their crystalline structure, BET for surface area, TGA to observe their metal core to surfactant ratio and ICP-OES for metal ratio concentrations. Figure 4-4 shows TEM images of varied ferrite nanocrystals at a fixed size which were produced by the decomposition of different metal oleates. TEM images show high quality of monodisperse nanocrystals. This method facilitated the creation of the libraries of various ferrite nanocrystals including manganese ferrite, nickel ferrite, cobalt ferrite and zinc ferrite. Typically, composition for the ferrite nanocrystals was 2:1, except for zinc ferrite since it was synthesized from the decomposition of an iron-zinc complex where the iron to zinc ratio was 5:1 or 4:1.
Figure 4-4. TEM images of binary ferrite nanocrystals.
TEM images of bimetallic ferrite nanocrystals (A) Fe$_3$O$_4$, (B) MnFe$_2$O$_4$, (C) NiFe$_2$O$_4$, (D) ZnFe$_2$O$_4$ and (E) CoFe$_2$O$_4$.

XRD pattern shows that all ferrites correspond to the expected positions and peaks for magnetite (Figure 4-5). Magnetite reference is used since it is the simplest spinel ferrite. Before XRD measurement, all ferrites except for magnetite were placed in a furnace at 800°C for 12 h to remove organic content. The heating of the powders causes an increase in the crystallite size resulting in a higher resolution diffraction pattern. While the comparative, diffraction pattern for magnetite is clearly broadened. The structural comparison can be clearly observed.
Figure 4-5. XRD patterns of binary ferrite nanocrystals.
XRD patterns of binary ferrites. Red lines correspond to the expected peak positions and intensities for magnetite (JCPDS#190629).

For further structural elucidation. TGA and BET surface area measurements were performed for the five varied compositions on the dried powders. Although the organic coating was removed from the nanoparticles before analysis, there is still a large percentage of organic loss observed from TGA. Interestingly, surface area measured for magnetite and manganese ferrite measured from BET reveals high values. While the theoretical surface area should be approximately 100 m²/g, the experimental surface area demonstrates smaller values. This observed decrease is due to the aggregation that is caused when the coating or surfactant is removed.
<table>
<thead>
<tr>
<th>Composition</th>
<th>% metal oxide (TGA)</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄</td>
<td>57.5</td>
<td>65.5</td>
</tr>
<tr>
<td>MnFe₂O₄</td>
<td>57.1</td>
<td>63.6</td>
</tr>
<tr>
<td>NiFe₂O₄</td>
<td>50.6</td>
<td>10.2</td>
</tr>
<tr>
<td>CoFe₂O₄</td>
<td>45.5</td>
<td>15.8</td>
</tr>
<tr>
<td>ZnFe₂O₄</td>
<td>66.4</td>
<td>17.4</td>
</tr>
</tbody>
</table>

Table 4-1. Summary of BET and TGA for binary ferrites.
Table summarized surface area measured in BET and metal oxide percentage collected in TGA of binary ferrite nanoparticles.

4.3.2. Ternary ferrite nanocrystals

4.3.2.1. Synthesis of MnₓZnᵧFe₃-x-yO₄ nanocrystals

The mixture of iron- zinc oleate complex (from 0.5 to 2.5 mmol) and manganese oleate (from 0.25 to 1.25 mmol) were used with 3 mmol of oleic acid in 10 g of 1-octadecene 315°C for 2 h.

4.3.2.2. Synthesis of CoₓZnᵧFe₃-x-yO₄ nanocrystals

The mixture of iron- zinc oleate complex (from 0.5 to 2.5 mmol) and cobalt oleate (from 0.25 to 1.25 mmol) were used with oleic acid (from 1.5 to 7.5 mmol) in 1-octadecene (from 5 to 15 g) 315°C for 2 h.
4.3.2.3. Synthesis of Co$_x$Ni$_y$Fe$_{3-x}$O$_4$ nanocrystals

The mixture of iron- nickel oleate complex (1 mmol) and cobalt oleate (0.1 mmol) were used with 3 mmol of oleic acid in 10 g of 1-octadecene 315°C for 2 h.

4.3.2.4. Synthesis of Mn$_x$Co$_y$Fe$_{3-x}$O$_4$ nanocrystals

The mixture of iron oleate (1 mmol), manganese oleate (0.5 mmol) and cobalt oleate (0.1 mmol) were used with 3 mmol of oleic acid in 10 g of 1-octadecene 315°C for 2 h.

4.3.2.5. Ternary ferrite nanocrystals characterization

The ternary ferrites were characterized in the same manner as already described above. Figure 4-6 shows TEM images of four different compositions synthesized at a fixed size. The images again illustrate the high quality of monodisperse nanocrystals attained, confirming the robust nature of this synthetic methodology. The metal ratio for ferrite nanocrystals was measured from ICP-OES.
TEM images of ternary ferrites. TEM images of ternary ferrite nanocrystals (A) $\text{Co}_{0.2}\text{Ni}_{0.6}\text{Fe}_{2.2}\text{O}_4$, (B) $\text{Co}_{0.7}\text{Zn}_{0.2}\text{Fe}_{2.1}\text{O}_4$, (C) $\text{Mn}_{0.6}\text{Co}_{0.1}\text{Fe}_{2.3}\text{O}_4$ and (D) $\text{Mn}_{0.9}\text{Zn}_{0.3}\text{Fe}_{1.8}\text{O}_4$.

X-ray powder diffractions show that all ferrites match with magnetite peaks positions (Figure 4-7). No impurity peaks are observed in the patterns. The broadness in the diffraction peaks suggests that the particles are in the nanosize range.
Figure 4-7. XRD patterns of ternary ferrites.
XRD diffractorgrams of ternary ferrite nanocrystals. Red lines correspond to the expected peak positions and intensities for magnetite.

TGA for ternary ferrites was performed to assess the organic content in the nanoparticles. Also, BET surface area was measured and results show very similar values for all compositions at a fixed size suggesting that degree of aggregation in these samples is very similar. Table 4-2 summarizes TGA and BET data collected for ternary ferrites.
<table>
<thead>
<tr>
<th>Composition</th>
<th>% metal oxide TGA</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn₀.₉Zn₀.₃Fe₁.₈O₄</td>
<td>77.8</td>
<td>23.1</td>
</tr>
<tr>
<td>Co₀.₇Zn₀.₂Fe₂.₁O₄</td>
<td>50.5</td>
<td>17.5</td>
</tr>
<tr>
<td>Mn₀.₆Co₀.₁Fe₂.₃O₄</td>
<td>79.03</td>
<td>27.4</td>
</tr>
<tr>
<td>Co₀.₂Ni₀.₆Fe₂.₂O₄</td>
<td>62.3</td>
<td>26.4</td>
</tr>
</tbody>
</table>

Table 4-2. Summary of BET and TGA data.  
Table summarizes surface area measured in BET and metal oxide percentage collected in TGA for ferrite nanocrystals.

4.3.3. Nanocrystal composition effect on magnetic properties

Spinel ferrites $\text{MFe}_2\text{O}_4$ ($\text{M}=\text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$ and $\text{Zn}^{2+}$) offer the ability to tune the magnetic properties because of the inclusion of varying transition metals ions to structure rather than only $\text{Fe}^{2+}$ ions. The introduction of new ions produces inter- sublattice super exchange interactions between A and B sites. The cation distribution depends on the electronic configuration and valence state.¹⁸³ For example, cobalt ferrite, $\text{CoFe}_2\text{O}_4$ has been greatly being studied because of the phenomenal magnetic properties they exhibit in the bulk state.¹⁹⁰ Cobalt ferrite crystallized in an inverse spinel structure is represented as $(\text{Co}^{2+}•\delta \text{Fe}^{3+}•\nu -\delta)\text{A} [\text{Co}^{2+}•\nu -\delta \text{Fe}^{3+}•\nu •\delta] \text{B} \text{O}_4$ and displays large magnetization since cobalt ferrite is known to have the highest degree of inversion with most $\text{Co}^{2+}$ ions in the octahedral sites.¹⁹¹,¹⁹² In addition, site preference of ions depends on their ionic radii and the size of the interstices. Therefore, trivalent ions prefer to occupy tetrahedral sites and divalent ions prefer to occupy octahedral sites which can further be utilized in designing improved magnetic properties.²⁶
In most of the ternary ferrites synthesized zinc was added as the third metal to the iron crystal structure. Zinc ions were chosen since it causes a redistribution of metal ions between tetrahedral and octahedral sites which produces higher interactions between magnetic spins centers. Rath et al. reported a study of nanosized Mn-Zn ferrites. They found that magnetic properties of ferrite depended on the distribution of cations in the two sites available. They demonstrate that cation distribution was consequence of two processes which involve the strong chemical affinity of certain cations to occupy inequivalent sites, A or B sites and the metastable cation distribution in nanoparticles. Arulmurugan et al. synthesized $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ and $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ with $x$ varying from 0.1 to 0.5. They found that magnetic properties strongly depended on zinc substitution due to the influence of cationic stoichiometry and their occupancy in A or B sites. Their experimental data revealed that high magnetization is observed for low concentrations of zinc. Vaidyanathan et al. expanded on the synthesis of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ with $x$ varying from 0.1 to 1.0. Their experimental data showed similar results as previously reported where highest saturation magnetization was observed at low zinc substitution. Thus, magnetic studies of different compositions were performed to observe the possible increase on their magnetic response when modifications in composition are performed. The zinc substitution was performed as low as possible since reported studies demonstrated highest saturation magnetization at low zinc substitution.
Magnetization data was collected for binary ferrite nanocrystals. An essential characteristic of magnetic materials to be viable as contrast agents is to exhibit a superparamagnetic response when external magnetic field is applied. This property allows for a quick response in low applied field and no hysteresis (no coercivity) is observed. The particles must be kept in the superparamagnetic regime as any remnant magnetization will interfere with the magnetic susceptibility resulting in a useless material which would not function as a contrast agent. Hysteresis loop at room temperature shows that all ferrites behave as superparamagnetic materials due to the lack of coercivity (Figure 4-8A). Initial magnetic susceptibility of ferrites was measured from at low fields. The samples were measure in solution at 0.1% by volume in kerosene (Figure 4-8B). As predicted, zinc ferrite is the nanocrystal that exhibits the largest magnetic response. This finding confirms that by varying the composition of iron oxides higher magnetic susceptibilities can be attained. For the other compositions, it is possible that as size is modified higher susceptibilities can be seen.
Figure 4-8. Magnetic data for binary ferrites. (A) Hysteresis curve at 300K and (B) magnetization versus applied field for binary ferrites. Measurements were performed at 0.1% by volume in kerosene. Samples were measured in SQUID.

Initial susceptibilities were measured at room temperature for ternary ferrites at 0.5% by volume in kerosene (Figure 4-9). Data indicates that at a fixed size, cobalt zinc ferrite has the highest magnetic susceptibility. This confirms that the doping of zinc causes an increase in magnetization due to the redistribution of cations in the crystal structure. Since cobalt zinc ferrite had the highest magnetic response a size dependent study was performed to understand their magnetic behavior and find the ideal size for this composition.
Figure 4-9. Magnetic data for ternary ferrite nanocrystals. Magnetization versus applied field of ternary ferrites at room temperature. Samples were measured at 0.5% by volume in kerosene. Data was collected in SQUID.

The unique magnetic characteristic of these superparamagnetic particles is that they can exhibit properties similar to a ferromagnetic or to a paramagnetic material depending on the temperature. As described below, below a critical threshold, the blocking temperature ($T_B$) a permanent dipole is achieved with behavior more similar to that of a ferromagnet where there is remnant magnetization at zero field. Above the $T_B$, the particle can exhibit the rapid magnetization in low fields giving rise to the superparamagnetism. Through the superparamagnetic relaxation, above the $T_B$, there is no remnant magnetization at zero field. Therefore, it is necessary to understand the blocking temperature and design a system where the operating conditions are above this so as to remain in
the superparamagnetic regime. Temperature dependent magnetization data was measured for binary ferrite nanoparticles (Figure 4-10). Zero-field cooled (ZFC) was measured by cooling the sample down to 5 K without an applied field (open squares). After 5 K has been reached, magnetization is measured when a field of 100 Oe is applied and temperature is raised up to 380 K. At 5 K, magnetization is very low but as temperature rises, magnetization starts to increase until it reaches a maximum and then starts to decrease. Field-cooled (FC) was collected by cooling the samples to 5 K under an applied magnetic field of 100 Oe (closed squares). ZFC-FC curves support the understanding of superparamagnetic behavior of nanoparticles. Superparamagnetic relaxation is related with the magnetic anisotropy of nanoparticles. In a single domain system all magnetic moments align to a preferred axis of orientation the “easy axis” when a magnetic field is applied below the Curie temperature. The easy axis is the direction in which a crystal quickly aligns when a magnetic field is applied. This easy axis is defined by the coupling between electron spins and its orbital angular momentum.\textsuperscript{17} Anisotropy energy also known as magnetocrystalline anisotropy is produced from these couplings.\textsuperscript{17,98} The magnetocrystalline anisotropy for a single domain particle can be calculated using Equation 4-1, where K is the magnetocrystalline anisotropy constant, V is the volume of the particle and $\theta$ is the angle between the magnetization and the easy axis. This gives rise to the energy barrier that must be overcome to move the particles from a ferromagnetic state into the superparamagnetic state.
\[ E_A = KV\sin^2 \theta \]

**Equation 4-1. Magnetocrystalline anisotropy**

Magnetization was measured as temperature was raised to 380 K. FC curves show that the maximum always occurs at 5 K and slightly decreases as temperature is increased. The decreasing of temperature in ZFC curves causes the potential energy to settle to a minimum by aligning the magnetization of particles along the easy axis. In ZFC curves the lowest magnetization is observed at 5 K. As temperature is increased in the presence of an applied field, energy barriers are surpassed and induce the initiation of superparamagnetic relaxation. Also, total magnetization increases as the temperature is increased until a maximum is attained, \( T_B \). This temperature is where thermal activation has overcome all energy barriers. When all nanoparticles are exhibiting superparamagnetic relaxation, the magnetization follows the Curie Law where it starts decreasing as temperature is increased.\(^{17}\) In the FC curves, nanoparticles are frozen in the direction of the applied field. The highest magnetization is observed at 5 K. When the nanoparticles are thermally activated the magnetization stays at the applied magnetic field. Above the blocking temperature, nanoparticles still retain the superparamagnetic relaxation effect observed in ZFC which causes an overlap of ZFC and FC curves.

ZFC-FC curves reveal that when ZFC reached the maximum (blocking temperature) it overlaps with FC curve. This overlapping signifies that the size distribution of the nanoparticles for all compositions is pretty narrow, which is ideal for contrast agent applications since all nanoparticles will exhibit the same
magnetic response. In the case where the maximum of ZFC is not overlapped with FC it signifies that the nanoparticles analyzed have a wide size distribution. The blocking temperatures for magnetite, manganese ferrite, nickel ferrite, cobalt ferrite and zinc ferrite are 154 K, 115 K, 115 K, 350 K, and 144 K, respectively. Cobalt ferrite shows a blocking temperature of 350K that is much higher than other ferrites explored. This is not surprising as cobalt ferrite is known to be hard magnet (large coercivities, slow relaxation) in the bulk state, where a much higher input of energy (higher magnetic fields) is needed to overcome the energy barrier.

![Figure 4-10. ZFC-FC curves for binary ferrite nanocrystals.](image)

Temperature dependence of the magnetization for zero-field-cooled (ZFC) and field-cooled (FC) binary ferrites under a magnetic field of 100 Oe.
4.3.4. Nanocrystal size effect on magnetic properties

As previously discussed in Chapter 1, size of nanocrystals has a substantial effect on the magnetic properties of nanocrystals.\textsuperscript{99,100,101} There are three magnetic regimes where nanocrystals can be depending on their size. Typically, bulk materials are in the multi domain regime, where multiple magnetic arrays are separated by domain walls. The appearance of domain walls reduces magnetostatic energy in the nanocrystal thus coercivity is not very large. As size further decreases, single domain is reached. Magnetic moments will have a locked stable direction of magnetization. In single domain regimes all magnetic moments rotate coherently when a magnetic field is applied. Lastly, when size of the nanocrystals is below the critical size they reach superparamagnetic regime. In this stage, nanocrystals can easily change direction of magnetization due to the unstable magnetic spins they possess in the absence of an external field. As mentioned in Chapter 1, this behavior of nanocrystals is ideal for imaging purposes due to their rapid magnetization with an applied magnetic field and the lack of coercivity nanocrystals exhibit. Therefore, an important feature of nanoparticles to be used as potential contrast agents is that they need to have a superparamagnetic response as magnetic field is applied. Hysteresis data at room temperature was collected for liquid samples of 0.5% by volume of iron oxide nanocrystals (Figure 4-11A). It can be observed that the three sizes analyzed for iron oxide behave as superparamagnetic because no coercivity is observed. In addition, initial magnetic susceptibility for the three sizes was collected and it was found that 20 nm iron oxide nanocrystal has the highest initial magnetic susceptibility (Figure 4-11B).
Hence, for iron oxide nanocrystals the “ideal size” would be approximately 16 nm. Above 16 nm, the nanocrystals begin to move into a transition state from superparamagnetic to single domain regime where much higher fields are needed to magnetize larger sizes.

![Figure 4-11. Magnetic data for iron oxide nanocrystals.](image)

(A) Hysteresis curve at 300K and (B) magnetization versus applied field at 300K. Measurements were performed in solution at 0.5% by volume in kerosene. Data was measured in SQUID.

Varied sizes of zinc ferrite nanocrystals were also studied on the effect on their magnetic properties. Increasing the concentration of the metal precursor resulted in varied sizes of zinc ferrites. The metal to surfactant ratio was kept 1:3 for all synthesized ferrites Figure 4-12 illustrates TEM images of four different sizes of zinc ferrites. It can be observed the high quality of nanocrystals with a dispersity of less that 10%. Sizes of these nanocrystals range from 10 to 20 nm.
Zinc ferrite is an interesting material since in the bulk state they exhibit very small magnetization values because of being a normal spinel. Zn$^{2+}$ ions occupy A-sites (tetrahedral sites) and Fe$^{3+}$ ions occupy B-sites (octahedral sites) which exhibits small overall magnetization.\textsuperscript{102,38} In the nanoscale, there is a redistribution of ions where the normal spinel changes to mixed spinel. Therefore, Fe$^{3+}$ ions and Zn$^{2+}$ are distributed over A and B sites.\textsuperscript{103} This redistribution leads to an increase in magnetization due to an increase of spins involved in the ferrimagnetic ordering of the material which originates from the strong inter-sublattice (A-B) super exchange interaction as opposed to the intra-sublattice (A-A and B-B) interactions.\textsuperscript{80} Magnetization data was measured for sample solution of 0.5\% by volume in kerosene. Figure 4-13A shows the hysteresis curves at room
temperature for the four different sizes synthesized of zinc ferrite. It was found that all sizes show a superparamagnetic behavior since no coercivity is observed. Initial magnetic susceptibility was collected at low fields at room temperature and it is observed that 13 nm zinc ferrite has the highest initial magnetic susceptibility (Figure 4-13B). Above 13 nm the magnetic susceptibility starts to decrease probably due to the transition of magnetic behavior. Therefore, much higher fields are needed to magnetize and align the magnetic spins for larger sizes.

![Figure 4-13. Magnetic data for zinc ferrite nanocrystals.](image)

(A) Hysteresis curve at 300K and (B) magnetization versus applied field of zinc ferrites at 300K. Measurements were performed at 0.5% by volume in kerosene. Data was collected in SQUID.

Lastly, a size dependent study for cobalt-zinc ferrite was explored since this composition exhibited the highest magnetic susceptibility at a fixed size. Five different sizes were synthesized from 7 to 30 nm. Data from ICP, shows that metal composition was successfully kept constant, $\text{Co}_{0.3}\text{Zn}_{0.2}\text{Fe}_{2.5}\text{O}_4$, except for the smallest size attained where the cobalt concentration was increased and zinc
concentration was reduced, $\text{Co}_{0.6}\text{Zn}_{0.1}\text{Fe}_{2.5}\text{O}_4$. It was not possible to obtain higher composition of zinc for small sizes possibly because zinc atoms have a larger atomic size and it becomes harder to incorporate the metal cations into the crystal structure. Figure 4-14, shows TEM images of CoZn ferrites where it is observed the monodispersity of the nanocrystals.

Figure 4-14. TEM images of cobalt zinc ferrites.
TEM images of cobalt- zinc ferrites (A) 7.2, (B) 10.4, (C) 19.7, (D) 23.3 and (E) 29.6 nm.

The partial replacement of cobalt ions for non-magnetic zinc ions can potentially increase the magnetization of nanomaterials as zinc ions will occupy octahedral sites. The replacement of ions will produce an increase in the total moment because of the decreased population in the tetrahedral sites. Magnetic
characterization was performed for all different sizes of Co-Zn ferrite at a concentration of 0.1% by volume in kerosene. It is seen that all nanocrystals develop a superparamagnetic behavior which is ideal for imaging purposes (Figure 4-15A). Magnetic susceptibility data indicates that the smallest CoZn ferrite is the one that has the highest magnetic susceptibility (Figure 4-15B). As size increases, there is a decrease in magnetic susceptibility. Magnetic susceptibility was very extremely low for the smallest size thus; it was not be possible to collect magnetic data at low fields.

![Figure 4-15. Magnetic data for cobalt zinc ferrite nanocrystals.](image)

(A) Hysteresis curve at 300K and (B) magnetization versus applied field of cobalt-zinc ferrites. Measurements were performed in solution at 0.1% by volume in kerosene. Data was measured in SQUID.

Table 4-3 displays a summary of the magnetic susceptibilities of varied ferrites with varied compositions. Also, susceptibilities have been normalized to
2% by volume since this concentration was used for comparison with all other magnetic nanoparticles.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Size (nm)</th>
<th>%v/v</th>
<th>(\chi_v) at 300K SQUID</th>
<th>(\chi_v) normalized 2% v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(_3)O(_4)</td>
<td>10.4</td>
<td>0.5</td>
<td>0.064</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>16.3</td>
<td>0.5</td>
<td>0.078</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>27.4</td>
<td>0.5</td>
<td>0.047</td>
<td>0.19</td>
</tr>
<tr>
<td>MnFe(_2)O(_4)</td>
<td>8</td>
<td>1.0</td>
<td>0.0065</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.0</td>
<td>0.0099</td>
<td>0.20</td>
</tr>
<tr>
<td>Ni(_0.9)Fe(_2.1)O(_4)</td>
<td>10.5</td>
<td>0.1</td>
<td>0.0001</td>
<td>0.002</td>
</tr>
<tr>
<td>Co(<em>{1.2})Fe(</em>{1.8})O(_4)</td>
<td>10.4</td>
<td>0.1</td>
<td>0.0054</td>
<td>0.11</td>
</tr>
<tr>
<td>Zn(<em>{0.4})Fe(</em>{2.6})O(_4)</td>
<td>10.4</td>
<td>0.1</td>
<td>0.0075</td>
<td>0.15</td>
</tr>
<tr>
<td>Zn(<em>{0.5})Fe(</em>{2.5})O(_4)</td>
<td>10.8</td>
<td>0.5</td>
<td>0.025</td>
<td>0.10</td>
</tr>
<tr>
<td>Zn(<em>{0.4})Fe(</em>{2.6})O(_4)</td>
<td>13.7</td>
<td>0.5</td>
<td>0.049</td>
<td>0.20</td>
</tr>
<tr>
<td>Zn(<em>{0.4})Fe(</em>{2.6})O(_4)</td>
<td>15</td>
<td>0.5</td>
<td>0.016</td>
<td>0.06</td>
</tr>
<tr>
<td>Zn(<em>{0.2})Fe(</em>{2.8})O(_4)</td>
<td>20.9</td>
<td>0.5</td>
<td>0.0072</td>
<td>0.03</td>
</tr>
<tr>
<td>Co(<em>{0.6})Zn(</em>{0.1})Fe(_{2.3})O(_4)</td>
<td>7.2</td>
<td>0.1</td>
<td>0.0093</td>
<td>0.19</td>
</tr>
<tr>
<td>Co(<em>{0.6})Zn(</em>{0.1})Fe(_{2.3})O(_4)</td>
<td>10.4</td>
<td>0.1</td>
<td>0.0087</td>
<td>0.17</td>
</tr>
<tr>
<td>Co(<em>{0.6})Zn(</em>{0.1})Fe(_{2.3})O(_4)</td>
<td>19.7</td>
<td>0.1</td>
<td>0.0018</td>
<td>0.054</td>
</tr>
<tr>
<td>Co(<em>{0.6})Zn(</em>{0.1})Fe(_{2.3})O(_4)</td>
<td>23.3</td>
<td>0.1</td>
<td>0.0008</td>
<td>0.016</td>
</tr>
<tr>
<td>Co(<em>{0.7})Zn(</em>{0.2})Fe(_{2.1})O(_4)</td>
<td>10</td>
<td>0.5</td>
<td>0.0245</td>
<td>0.098</td>
</tr>
<tr>
<td>Co(<em>{0.1})Zn(</em>{0.3})Fe(_{2.6})O(_4)</td>
<td>15</td>
<td>0.5</td>
<td>0.097</td>
<td>0.39</td>
</tr>
<tr>
<td>Co(<em>{0.2})Zn(</em>{0.4})Fe(_{2.4})O(_4)</td>
<td>25</td>
<td>0.5</td>
<td>0.019</td>
<td>0.078</td>
</tr>
<tr>
<td>Composition</td>
<td>Size (nm)</td>
<td>%v/v</td>
<td>χᵥ at 300K SQUID</td>
<td>χᵥ normalized 2% v/v</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------</td>
<td>------</td>
<td>-----------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>Mn₀.₆Co₀.₁Fe₂.₃O₄</td>
<td>10</td>
<td>1.0</td>
<td>0.005</td>
<td>0.01</td>
</tr>
<tr>
<td>Co₀.₆Ni₀.₁Fe₂.₃O₄</td>
<td>10</td>
<td>1.0</td>
<td>0.084</td>
<td>0.17</td>
</tr>
<tr>
<td>Co₀.₆Ni₀.₁Fe₂.₃O₄</td>
<td>13</td>
<td>1.0</td>
<td>0.0008</td>
<td>0.0016</td>
</tr>
<tr>
<td>Mn₀.₉Zn₀.₃Fe₁.₈O₄</td>
<td>10</td>
<td>0.5</td>
<td>0.0032</td>
<td>0.013</td>
</tr>
<tr>
<td>Mn₀.₅Zn₀.₅Fe₂O₄</td>
<td>13</td>
<td>0.5</td>
<td>0.045</td>
<td>0.18</td>
</tr>
<tr>
<td>Mn₀.₇Zn₀.₄Fe₁.₉O₄</td>
<td>20</td>
<td>0.5</td>
<td>0.079</td>
<td>0.31</td>
</tr>
</tbody>
</table>

**Table 4-3. Summary of ferrites in solution.**
Table summarizes magnetic susceptibilities of ferrite nanocrystals dispersed in kerosene at volume concentration measured. Also, magnetic susceptibilities have been normalized to 2% by volume. Data was collected in SQUID.

The size dependent studies performed for the varied compositions show that there is a sweet spot of size for each composition of nanoparticles. For all ferrites analyzed except for cobalt zinc ferrite, below a critical size leads to a small magnetic response and above a threshold large the particle becomes single domain which demands higher fields to magnetize the nanoparticles and results in low magnetization at low fields. This suggests that the ideal size for all compositions is in the limit of the superparamagnetic-single domain.
4.4. Non-interacting superparamagnetic model: fit of M versus H measurements

Colloidal magnetic nanoparticles are typically coated with polymers or surfactants that prevents them from aggregation. Non-interacting magnetic nanoparticles are of great interest for many applications.\textsuperscript{104} When an external magnetic field is applied each nanoparticles aligns independently in the direction to the magnetic field and they do not retain any magnetization (no hysteresis) when the field is removed, showing a superparamagnetic behavior. One interesting effect that magnetic nanoparticles can exhibit is the presence of a magnetically dead surface layer which does not contribute to the magnetic moment of the particle. The easiest method used to describe non-interacting superparamagnetic nanoparticles is the Langevin equation (discussed in Chapter 1) and facilitates the estimation of the effective magnetic size of nanocrystals.\textsuperscript{105,75} The total magnetization of the colloidal dispersion is given by Equation 4-2.

\[ M = \chi H + \frac{\rho C m}{\mu_0} \left( \coth \left( \frac{mH}{k_B T} \right) - \frac{k_B T}{mH} \right) \]

Equation 4-2. Formula for fitting experimental data for magnetization

\( \chi \) is the magnetic susceptibility (dimensionless), H is the magnetic field, \( \rho \) is the density of the nanoparticle, C is concentration of colloidal solution (N/L), is the magnetic dipole moment, \( \mu_0 \) is the permittivity of vacuum, and \( k_B T \) is the thermal energy. The magnetic particle size was calculated from the measured hysteresis loops. Typically, concentrations used for the magnetic measurements were 0.5 %
by volume or less because higher concentrations would begin to exhibit magnetization for dipolar chains rather than single particles.\textsuperscript{106,107} The magnetic core size for most ferrites analyzed is smaller than the obtained from TEM because of the presence of nonmagnetic or magnetically dead layer on the surface of nanoparticles.\textsuperscript{108} Hysteresis loops were collected for iron oxide and binary ferrite diluted samples assuming they were non-interacting particles at room temperature. Figure 4-16 shows hysteresis loop for 16.3 nm magnetite solution and its corresponding fit. Magnetic size resulted in 15.6 nm. The small difference in between TEM size and calculated magnetic size comes from surface defects in the crystal structure.\textsuperscript{109}

![Graph](image)

**Figure 4-16. Fitted data for iron oxide nanocrystal.**
Magnetization versus applied field at room temperature for 16.3 nm colloidal magnetite and the corresponding fit.
Table 4-4 summarizes the average diameters from TEM and diameter from magnetic measurements. It is noted that magnetic size calculated from magnetic data is slightly smaller than the average size measured from TEM. This is an indication that a small magnetic dead layer exists in the nanoparticles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d_{\text{TEM}}$ (nm)</th>
<th>$d_{\text{magnetic}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$</td>
<td>10.4</td>
<td>10.3</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>16.3</td>
<td>15.6</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>27.4</td>
<td>21.6</td>
</tr>
<tr>
<td>MnFe$_2$O$_4$</td>
<td>10.4</td>
<td>8.9</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>10.5</td>
<td>8.6</td>
</tr>
<tr>
<td>ZnFe$_2$O$_4$</td>
<td>10.4</td>
<td>9.8</td>
</tr>
</tbody>
</table>

Table 4-4. Summary of average sizes from TEM and magnetic data for diluted isolated magnetic nanoparticles.

Table summarizes sizes of magnetic nanoparticles measured from TEM images and magnetic size calculated from fitting magnetization curves using Langevin function.

4.5. Effect of particle aggregation

Magnetic properties of nanoparticles are strongly governed by the interparticle interactions. The two major interparticle interactions on superparamagnetic systems are dipolar and exchange interactions.$^{110}$ It is well known that in diluted systems the major interparticle interactions are dipolar
interactions because of the local field that neighboring dipoles of particles create.\textsuperscript{111} The effect of particle aggregation was studied to observe if there was an enhancement effect on the magnetic properties of the nanoparticles since the strength of interparticle interactions was expected to significantly change the magnetic properties. Nanocrystals synthesized via thermal decomposition method were the first materials that were studied. Nanoparticles synthesized through this method are coated by oleates bound to the surface of available ions. This coating helps nanoparticles to be non-interacting particles; thus exhibit dipole-dipole interactions between them. In order to create aggregates of these particles it is necessary to remove the organic coating they possess. This procedure was achieved as described below.

Five milliliters of a concentrated nanocrystal solution (in hexane) was added to a 50 mL centrifuge tube. Hexane was evaporated using N\textsubscript{2}. A 12 mL syringe was used to collect 5 mL of Super-Hydride solution (1.0 M lithium triethylborohydride in THF). Super-hydride is tremendously reactive therefore water and humidity in the working area must always be avoided. This process was performed in a chemical hood equipped with a face shield, safety glasses and chemically resistant gloves. The super-hydride solution was added drop by drop through a 0.2 μm PES filter which replaced the needle. As the super-hydride was added an exotherm and gas evolution was observed in the solution possibly due to the release of hydrogen. Once the reaction solution stopped bubbling, the centrifuge tube was closed and placed in a sonicating bath for 15 minutes. Then, 20 mL of ethanol were slowly added super slowly to the centrifuge tube causing again a gas evolution in the
solution which was placed again placed in the sonicator for 15 minutes. Acetone was used to bring the volume to 45 mL and the solution was centrifuged at 6,000 rpm for 15 min. This process was repeated three times or until no more bubbling was observed. The final product was dried in a vacuum oven overnight at 80°C.

Iron oxide nanocrystals synthesized via thermal decomposition method were the first nanoparticles where comparison between solutions and aggregates of same size and same composition was performed. The organic coating was removed from iron oxide nanocrystal solutions of 10, 16 and 27 nm following the previously discussed procedure. Figure 4-17A shows magnetite sample in solution close to a magnet. Figure 4-17B shows magnetite powder sample after the removal of the surface coating of the nanoparticles. In both physical states, magnetite is observed to be magnetic since nanoparticles are attracted when a magnet is in close contact. Magnetic data of these different conditions of iron oxide nanocrystals show higher initial magnetic susceptibilities for the powder samples when compared with samples of the same composition and sizes in solution (Figure 4-17C). This could be explained from the different type of interparticle interactions present in each physical state of the material. In coated nanocrystals, the interparticle distance is too large for exchange interactions. Thus, dipolar interactions becomes the primary type of interparticle interaction since they act over longer ranges and are the strongest for diluted samples.\textsuperscript{112} However, for solid materials the exchange interactions have a strong effect and are dominant over the effect on magnetization because they are short-ranged interactions.
Figure 4-17. Comparison of iron oxide in solution versus aggregated nanoparticles.

(A) Magnetite sample in solution, (B) magnetite sample in powder and (C) magnetization versus applied field at 300K of magnetite aggregates (powders) and magnetite solutions at 0.5% by volume in kerosene. Data was collected in SQUID.

Moreover, three different compositions of ferrites were analyzed in powder to observe if there was an increase in the magnetic susceptibility. The coating of the nanocrystals was removed as previously discussed with super-hydride solution. Magnetic data for magnetite, manganese and zinc ferrite was collected at room temperature for powder samples. Figure 4-18A shows that all nanocrystals still behave as superparamagnetic materials, no coercivity is observed, remaining ideal for imaging purposes. Magnetization versus applied field at low fields shows the magnetic susceptibilities of ferrites at room temperature (Figure 4-18B). It is observed that ZnFe$_2$O$_4$ exhibits the highest magnetic susceptibility at room temperature.\textsuperscript{113,114} The low degree of inversion in manganese ferrites are likely the
cause could the one responsible for the significant difference on the magnetic susceptibilities between manganese and zinc ferrites.\textsuperscript{115}

Based on the higher magnetic susceptibilities observed, powders from different synthetic routes were synthesized and characterized to observe if there was any difference on their magnetic response. Coprecipitation method is a well known synthetic method which one of the advantages is that it is an aqueous synthesis. Therefore, no further surface modification is needed when the applications are water-based. Magnetite, manganese and zinc ferrites were synthesized following the coprecipitation methodology described in Chapter 2. Samples were dried and magnetic data was measured for each powder. Hysteresis curves at room temperature for all compositions highlights that the nanoparticles

\textbf{Figure 4-18. Magnetic data for ferrite nanocrystals synthesized via thermal decomposition.}
(A) Hysteresis curve at 300K and (B) magnetization versus applied field at 300K for ferrites synthesized via thermal decomposition method. Samples were analyzed in powder.
are superparamagnetic (Figure 4-19A). Magnetic data collected at low fields indicates that manganese ferrite and magnetite result with the highest magnetic susceptibilities (Figure 4-19B). In this case, manganese ferrite had a much higher magnetic response than zinc ferrite possibly due to a lack of rearrangement of ions. This results show that zinc ferrite is most likely behaving as a normal spinel which results in low magnetization. However, an interesting finding is that the magnetic susceptibilities are lower than for nanoparticles synthesized through thermal decomposition method. This reassures that the synthetic methodology that has been used over this whole study is the best one since it produces high quality of nanoparticles and enhanced magnetic properties are observed.

![Magnetic data of ferrites synthesized via coprecipitation.](image)

(A) Hysteresis curve at 300K and (B) magnetization versus applied field at room temperature for ferrites synthesized through coprecipitation. Samples were analyzed in powder. Data was collected in SQUID.
Additionally, commercial ferrite nanoparticles were analyzed to observe their magnetic response at low fields. Physical characterization of commercial nanoparticles has been discussed in Chapter 3. Magnetic measurements were performed at room temperature for the nanopowders. Figure 4-20A shows the hysteresis curve at room temperature for all three commercial powders. It is observed that all show a superparamagnetic behavior since no coercivity is observed. Magnetic data was collected at low fields to calculate the initial magnetic susceptibility of each composition (Figure 4-20B). It is observed that MnZnFe$_2$O$_4$ has the largest magnetic susceptibility which correlates to already reported data.$^{116}$ Also, it is observed that not even commercial nanoparticles develop a higher magnetic susceptibility than synthesized ferrites via thermal decomposition method, restating that thermal decomposition synthetic method generates high quality materials.
Figure 4-20. Magnetic data collected for commercial nanoparticles in powder. (A) Hysteresis curve at 300K and (B) magnetization versus applied field at room temperature for commercial nanopowders. Powders were measured in SQUID.

Table 4-5 displays a summary of magnetic susceptibilities at room temperature for powder samples.
Table 4-5. Summary of magnetic susceptibilities for aggregated ferrite nanoparticles.
Table summarizes magnetic susceptibility of ferrite nanocrystals synthesized through thermal decomposition and coprecipitation and commercial nanoparticles.

Furthermore, to confirm the effect of the interparticle interactions which are mainly governed by the distance between magnetic cores, iron oxide nanocrystals were functionalized with different chain lengths of fatty acids (synthetic methodology has been discussed in Chapter 2). Saturated fatty acids (lauric acid, 12C, stearic acid, 18C, and behenic acid 22C) and an unsaturated fatty acid: oleic acid (18C) were used for surface modification. The iron oxide solutions were dried in an vacuum oven at 80°C. Magnetic data was collected for the dried iron oxide nanocrystals coated with different fatty acids at room temperature (Figure 4-21). Data shows that the shortest fatty acid (lauric acid, 12C) used for the coating of the
nanocrystals exhibits the highest magnetic susceptibility. This correlates with the assumption that the closer the magnetic cores the largest the interparticle interaction between nanocrystals; thus highest magnetic response.

![Graph showing magnetization versus applied field for iron oxide nanocrystals with varied coatings.](image)

**Figure 4-21. Magnetic data collected for iron oxide nanocrystals with varied coatings.**

Magnetization versus applied field of iron oxide nanocrystals coated with different chain lengths of fatty acids.

### 4.6. Conclusions

The synthesis of magnetic nanoparticles is of extreme interest for many biological applications and more recently in the oil and gas industry due to their unique properties they feature. One of the most interesting properties of magnetic nanomaterials is that they can exhibit superparamagnetic behavior.
Superparamagnetic nanomaterials are of great interest since they quickly become magnetized when an external field is applied, even at low fields. Also, they do not retain any magnetization when the field has been removed. Therefore, no interference from the nanoparticles would be produced when they are used.

In this chapter, the synthesis and characterization of monodisperse ferrite nanocrystals was studied and the effect of composition on the magnetic properties of nanoparticles was investigated. The substitution \( \text{Fe}^{2+} \) ions for other metals generated an enhancement on the magnetic properties of nanocrystals. The addition of zinc atoms was found to significantly increase the magnetization due to the redistribution of ions between the A and B sites. From all compositions explored, cobalt zinc ferrite exhibited the highest initial magnetic susceptibility at low fields. These ferrites have a mixed spinel structure; therefore display the highest magnetic response since zinc is non-paramagnetic and results in no reduction of the moment in the A sites.

In addition, size dependent studies were realized for the most promising compositions to find the ideal size, the size which would have the highest magnetic response. The ideal size was determined to be just below the single domain threshold where superparamagnetic behavior is observed with the highest possible number of spin centers and no magnetization would be retained when a magnetic field has been removed.

Finally, aggregation of nanoparticles was found to boost the magnetic properties of magnetic nanoparticles. These studies showed that powders exhibit a
much higher magnetic susceptibilities than diluted samples due to stronger interactions between magnetic nanoparticles. While increased magnetic susceptibilities were achieved in powder aggregates, a controlled aggregation study of ferrite nanoparticles demonstrated this could lead to a much higher increases in magnetic susceptibilities.
Chapter 5

Synthesis of ferrite nanoclusters via solvothermal route

5.1. Introduction

Chapter 4 illustrated the desired size and composition discrete ferrite nanoparticles for magnetic imaging applications. It was also observed that aggregation of these particles led to the improved magnetic properties. A major challenge with aggregation is that is typically uncontrolled and leads to a high polydispersity of the aggregates, which is not optimal for developing applications based on that technology. This chapter will demonstrate a synthetic approach to discrete clusters made of ferrite nanoparticles and the advantageous magnetic properties that arise due to the interparticle interaction.

Lately, a variety of methods have been used for the synthesis of cluster structures. These include self-assembly, cooperative assembly, microemulsion and
solvophobic interactions all requiring at minimum a two step process. Most recently, an improved on step the solvothermal route has been identified and will be employed herein for the development of the nanoclusters.\textsuperscript{117,118}

5.2. Synthesis of nanoparticles through solvothermal method

Typical synthesis of ferrite nanoclusters was carried out in a solvothermal system by modified reduction reactions between FeCl\textsubscript{3} and ethylene glycol. Solvents (ethylene glycol, diethylene glycol or their mixture) metal salts (FeCl\textsubscript{3} \cdot 6H\textsubscript{2}O, MnCl\textsubscript{2} \cdot 6H\textsubscript{2}O, NiCl\textsubscript{2} \cdot 6H\textsubscript{2}O, ZnCl\textsubscript{2}, CoCl\textsubscript{2} \cdot 6H\textsubscript{2}O), capping agents (PVP, PEG, PVA and citrate) and urea were added to a beaker and were stirred for 30 minutes or until the solution was completely homogenous. The mixture was transferred to a teflon- lined stainless- steel autoclave (50 mL). The autoclave was heated in an oven at 200° C for 24 h. Consequently, the reaction mixture was cooled down to room temperature.

For purification purposes, the products were washed three times with ethanol and water and later collected using a cubic magnet. The final product was dried in an oven at 70° C overnight.

The magnetic properties of nanoparticles are highly dependent on the particle size.\textsuperscript{118} Therefore, great efforts were made to vary the cluster size and primary particle size of nanoparticle building block. Modifications such as changing
the solvent, capping agent, the concentration of reactants, the reaction temperature and time were performed to obtain various sizes of ferrite nanoclusters.

Furthermore, attempts were made to dope the second and third metal into the cluster to study the influence of composition on their magnetic properties. These were accomplished by incorporating metal chloride salts into the solution that was heated in the oven. The ferrites synthesized through a solvothermal process were the following: \(\text{Mn}_x\text{Zn}_y\text{Fe}_{3-x-y}\text{O}_4\), \(\text{Ni}_x\text{Zn}_y\text{Fe}_{3-x-y}\), \(\text{Mn}_x\text{Fe}_{3-x}\text{O}_4\) and \(\text{Ni}_x\text{Fe}_{3-x}\text{O}_4\).

### 5.3. Physical characterization

The main characterization techniques for the nanoclusters were TEM an SEM for size, size distribution and shape, XRD to confirm the crystalline structure of iron oxide, TGA to calculate metallic core to surfactant ratio, BET for surface area and DLS to investigate hydrodynamic diameter and stability of iron oxide nanoclusters. Figure 5-1 shows SEM and TEM images of an iron oxide nanocluster. The nanocluster is a hierarchical structure composed of hundreds of small primary crystals. Also, it can be observed the high porosity of the material which was confirmed with BET.
Figure 5-1. SEM and TEM images of iron oxide nanoclusters.
SEM image and (B) and (C) TEM images of iron oxide nanoclusters.

XRD was performed in order to confirm the crystallinity of the nanoclusters (Figure 5-2A). All observed peaks agree with the magnetite pattern shown in red. In addition, TGA was performed to observe the organic loss of each sample. It can be observed from TGA analysis (Figure 5-2B) that there is a ~30% loss of organic material and also quantify the actual mass of iron oxide in each sample that contributes to the magnetic response. This will be further discussed in this chapter.
Figure 5-2. XRD patterns and TGA analysis of iron oxide nanoclusters. (A) XRD patterns of iron oxide nanoclusters. Red lines correspond to the expected peak positions. Red lines correspond to the expected peak positions and intensities for magnetite (JCPDS# 190629). (B) TGA analysis of iron oxide nanocrystals.

Moreover, the successful incorporation of other metals to the iron structure was achieved. Figure 5-3 shows some typical TEM images of the nanocrystal clusters of different compositions. Mn-ferrite, MnZn-ferrite, Ni-ferrite and Ni-Zn ferrite were synthesized. The doping of other metals can significantly influence the size of the primary particle and the cluster.
Figure 5-3. TEM images of ferrite nanoclusters.
TEM images of ferrite nanoclusters (A) Mn$_{0.3}$Fe$_{2.7}$O$_4$, (B) Ni$_{0.05}$Fe$_{2.95}$O$_4$, (C) Mn$_{0.29}$Zn$_{0.05}$Fe$_{2.66}$O$_4$ and (D) Ni$_{0.01}$Zn$_{0.05}$Fe$_{2.94}$O$_4$.

In the study of magnetic properties of materials (bulk and nano) it is crucial to correlate their magnetic behavior with the structure/composition of the material. Therefore, the nanoparticles were further characterized with XRD. Figure 5-4 shows the ferrite samples exhibit a crystalline nature to the particles. The experimental pattern has an excellent fit with the theoretical pattern obtained from JADE database which indicates purity and identity of the materials under investigation.
**Figure 5-4. XRD patterns of ferrite nanoclusters.**
XRD diffractograms of ferrite nanoclusters. Red lines correspond to the expected peak positions and intensities for magnetite (JCPDS#190629).

Table 5-1 summarizes all the physical characterization performed for ferrite nanoclusters. BET and TGA were collected to verify the surface area and percentage of metal oxide in the nanocrystals. From BET, large surface areas were observed which indicates that the nanoclusters are highly porous materials. In regards to the data collected from TGA, the percentage of metal oxide after the organic loss varied from 62.5-82.3. This percentage helped us to correct our magnetization values which will be discussed later in this chapter.
<table>
<thead>
<tr>
<th>Ferrite</th>
<th>Primary particle size (nm)</th>
<th>Cluster size (nm)</th>
<th>BET (m²/g)</th>
<th>TGA %MO</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnₐFe₂.₉₇O₄</td>
<td>5.2 ± 1.0</td>
<td>89 ± 11</td>
<td>121.8</td>
<td>77.5</td>
</tr>
<tr>
<td>Mn₀.₃Fe₂.₇O₄</td>
<td>5.4 ± 1.1</td>
<td>64 ± 9.7</td>
<td>115.9</td>
<td>73.0</td>
</tr>
<tr>
<td>Mn₀.₆Fe₂.₄O₄</td>
<td>4.9 ± 5</td>
<td>139 ± 21</td>
<td>92.9</td>
<td>64.1</td>
</tr>
<tr>
<td>Mn₀.₄Fe₂.₆O₄</td>
<td>4.6 ± 1.1</td>
<td>126 ± 18</td>
<td>249.1</td>
<td>62.5</td>
</tr>
<tr>
<td>Mn₀.₃Fe₂.₇O₄</td>
<td>5.6 ± 1.0</td>
<td>38 ± 7.1</td>
<td>116.5</td>
<td>73.4</td>
</tr>
<tr>
<td>Ni₀.₀₄Fe₂.₉₆O₄</td>
<td>6.1 ± 0.9</td>
<td>48 ± 7.7</td>
<td>164.2</td>
<td>74.7</td>
</tr>
<tr>
<td>Ni₀.₀₅Fe₂.₉₅O₄</td>
<td>6.4 ± 1.1</td>
<td>45 ± 6.4</td>
<td>131.3</td>
<td>81.7</td>
</tr>
<tr>
<td>Mn₀.₄Zn₀.₀₄Fe₂.₆O₄</td>
<td>6.5 ± 1.1</td>
<td>54 ± 7.6</td>
<td>129.9</td>
<td>71.3</td>
</tr>
<tr>
<td>Mn₀.₄Zn₀.₀₄Fe₂.₆O₄</td>
<td>5.9 ± 1.0</td>
<td>51 ± 8.4</td>
<td>154.7</td>
<td>72.2</td>
</tr>
<tr>
<td>Mn₀.₄Zn₀.₀₄Fe₂.₆O₄</td>
<td>5.9 ± 1.1</td>
<td>37 ± 5.2</td>
<td>143.5</td>
<td>68.1</td>
</tr>
<tr>
<td>Mn₀.₄Zn₀.₀₄Fe₂.₆O₄</td>
<td>5.4 ± 0.9</td>
<td>33 ± 5.1</td>
<td>135.5</td>
<td>70.4</td>
</tr>
<tr>
<td>Ni₀.₀₁Zn₀.₀₅Fe₂.₉₄O₄</td>
<td>4.5 ± 0.8</td>
<td>84 ± 12</td>
<td>113.2</td>
<td>72.0</td>
</tr>
<tr>
<td>Mn₀.₀₂Zn₀.₀₅Fe₂.₉₃O₄</td>
<td>4.8 ± 0.9</td>
<td>69 ± 10</td>
<td>107.9</td>
<td>75.3</td>
</tr>
<tr>
<td>MnₓFe₃₋ₓO₄</td>
<td>5.5 ± 1.2</td>
<td>69 ± 11</td>
<td>106.4</td>
<td>82.3</td>
</tr>
<tr>
<td>MnₓFe₃₋ₓO₄</td>
<td>6.2 ± 1.1</td>
<td>83 ± 12</td>
<td>107.6</td>
<td>79.9</td>
</tr>
<tr>
<td>MnₓZnₓFe₃₋ₓ₋ₓO₄</td>
<td>6.0 ± 1.0</td>
<td>49 ± 7.2</td>
<td>94.6</td>
<td>78.4</td>
</tr>
<tr>
<td>MnₓZnₓFe₃₋ₓ₋ₓO₄</td>
<td>5.6 ± 0.9</td>
<td>47 ± 8.1</td>
<td>131.9</td>
<td>77.9</td>
</tr>
</tbody>
</table>

**Table 5-1. Summary of ferrite nanoclusters.**

Table summarizes the ferrite nanoclusters with its corresponding cluster size, primary particle size, surface area analysis and metal oxide percentage measured from TGA.
One of the major concerns when dealing with these nanomaterials is whether they would be able to remain stable in hostile environments. For example, if they are used in the oil and gas industry as an imaging agent, they need to be able to withstand high pressures, high temperatures and high shearing force. In order to assess their strength, the nanocrystal clusters were treated with heating, sonication and centrifugation. Figure 5-5 shows the TEM images of the nanoclusters after they were treated to different environments. It can be observed that there is no change in the structure of the nanomaterial, indicating that the clusters are strong enough to survive harsh conditions of potential applications.

![Figure 5-5. TEM images of iron oxide nanoclusters in different environments. TEM images of iron oxide nanoclusters (A) original sample, (B) sample was heated at 100°C, (C) sample was sonicated and (D) sample was centrifuged at 11,000 rpm.]

### 5.4. Magnetic characterization

In order to determine the optimal particles for potential applications it was necessary to find the optimal size and composition for the desired magnetic properties. The magnetic nanoclusters were characterized primarily with SQUID magnetometry. Magnetic characterization performed was focused on the initial
magnetic susceptibility measured from 0 to 50 Oe and hysteresis measurements. Details of each measurement are further explained in Chapter 2. These measurements helped to determine the effects that composition and size have on the magnitude of the magnetic susceptibility. In order to obtain nanoparticles with high magnetic susceptibility the following magnetic properties were observed: 1) particles should behave as superparamagnetic materials (exhibit no coercivity at room temperature) and 2) have a strong and quick response to a low applied magnetic field.

5.4.1. Improved magnetic susceptibility in iron oxide nanoclusters

The first materials that were characterized were iron oxide nanoclusters. Figure 5-6 shows TEM images of iron oxide nanoclusters with different cluster size a primary particle size. Primary size ranges from 5.6 to 9.9 nm and cluster size ranges from 126 to 350 nm.
Figure 5-6. TEM images of iron oxide nanoclusters.
TEM images of iron oxide nanoclusters (A) cluster size: 126 nm, primary particle size: 9.9 nm, (B) cluster size: 206 nm, primary particle size: 6.0 nm and (C) cluster size: 350 nm, primary particle size: 5.6 nm.

Magnetic susceptibility and hysteresis curves were collected for these samples. Figure 5-7A shows the hysteresis curve at room temperature for the nanocluster and it was observed that the materials behave as superparamagnetic due to lack of coercivity. Figure 5-7B shows the initial magnetic susceptibility of the iron oxide nanoclusters. The magnetic susceptibilities seen in the iron oxides nanoclusters were much higher than the ones observed in isolated nanoparticles. This behavior can be explained due to the inter-particle interactions between each primary unit crystal in the cluster. The cluster with the best magnetic behavior was the smallest one from the ones analyzed. This finding demonstrated the magnetic susceptibility of iron oxide nanoclusters is highly dependent on the size of the cluster and the primary particle.
Figure 5-7. Magnetization data for iron oxide nanoclusters. (A) Hysteresis curve at room temperature and (B) magnetization versus applied field of iron oxide nanoclusters. Samples analyzed in powder. Approximately 5-8 mg of powder was used for analysis.

Substantial efforts were completed to tune the cluster size and primary size of nanoclusters to extensively investigate the influence of these two attributes on the magnetic susceptibility of clusters. The magnetic susceptibility of a large number of iron oxide nanoclusters was measured (Table 5-2). These results greatly improved the understanding on the magnetic behavior of iron oxide nanocrystals and provided foundation for design of clusters with higher magnetic susceptibilities.
<table>
<thead>
<tr>
<th>Fe₃O₄</th>
<th>Primary particle size (nm)</th>
<th>Cluster size (nm)</th>
<th>SQUID χ (SI) at 300K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>38 ± 6</td>
<td>312 ± 43</td>
<td>4.83</td>
</tr>
<tr>
<td>2</td>
<td>49 ± 9</td>
<td>287 ± 49</td>
<td>4.76</td>
</tr>
<tr>
<td>3</td>
<td>35 ± 5</td>
<td>324 ± 46</td>
<td>5.60</td>
</tr>
<tr>
<td>4</td>
<td>5.3 ± 1.1</td>
<td>308 ± 29</td>
<td>5.04</td>
</tr>
<tr>
<td>5</td>
<td>6.1 ± 1.3</td>
<td>342 ± 46</td>
<td>5.42</td>
</tr>
<tr>
<td>6</td>
<td>8.2 ± 1.5</td>
<td>294 ± 38</td>
<td>7.21</td>
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<tr>
<td>7</td>
<td>9.9 ± 1.6</td>
<td>125 ± 19</td>
<td>8.12</td>
</tr>
<tr>
<td>8</td>
<td>6.0 ± 1.4</td>
<td>206 ± 32</td>
<td>5.22</td>
</tr>
<tr>
<td>9</td>
<td>5.6 ± 1.2</td>
<td>350 ± 55</td>
<td>4.35</td>
</tr>
<tr>
<td>10</td>
<td>6.5 ± 1.3</td>
<td>436 ± 58</td>
<td>6.63</td>
</tr>
<tr>
<td>11</td>
<td>37 ± 8.7</td>
<td>263 ± 34</td>
<td>5.28</td>
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<tr>
<td>12</td>
<td>8.3 ± 1.6</td>
<td>63 ± 12</td>
<td>15.4</td>
</tr>
<tr>
<td>13</td>
<td>8.6 ± 1.4</td>
<td>71 ± 12</td>
<td>1.6</td>
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<tr>
<td>14</td>
<td>7.0 ± 1.2</td>
<td>93 ± 11</td>
<td>13.5</td>
</tr>
<tr>
<td>15</td>
<td>34 ± 8.2</td>
<td>293 ± 43</td>
<td>4.89</td>
</tr>
<tr>
<td>16</td>
<td>6.1 ± 1.3</td>
<td>90 ± 11</td>
<td>14.5</td>
</tr>
<tr>
<td>17</td>
<td>6.9 ± 1.6</td>
<td>74 ± 13</td>
<td>17.6</td>
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<tr>
<td>18</td>
<td>5.9 ± 1.5</td>
<td>63 ± 12</td>
<td>16.4</td>
</tr>
<tr>
<td>19</td>
<td>9.1 ± 1.4</td>
<td>99 ± 10</td>
<td>13.4</td>
</tr>
<tr>
<td>20</td>
<td>8.7 ± 1.1</td>
<td>77 ± 11</td>
<td>14.5</td>
</tr>
<tr>
<td>21</td>
<td>7.5 ± 1.6</td>
<td>58 ± 9.1</td>
<td>18.4</td>
</tr>
</tbody>
</table>
Table 5-2. Summary of magnetic susceptibilities of iron oxide nanoclusters. Table summarized the cluster size, primary particle size and magnetic susceptibility at room temperature measured in SQUID in powders for iron oxide nanoclusters. Approximately 5-8 mg of sample was used for each measurement.

<table>
<thead>
<tr>
<th>Fe₃O₄</th>
<th>Primary particle size (nm)</th>
<th>Cluster size (nm)</th>
<th>SQUID $\chi$ (SI) at 300K</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>7.6 ± 1.5</td>
<td>49 ± 4.9</td>
<td>19.7</td>
</tr>
</tbody>
</table>

Figure 5-8 shows a 3D colormap surface of iron oxide nanoclusters to visualize the effect that primary size and cluster size have on the magnetic susceptibility. It is clearly demonstrated that a small primary particle size in the cluster will result in a higher magnetic response. Regarding cluster size, it is perceived that below 100 nm magnetic susceptibility starts to increase. This is encouraging in the sense that smaller nanoparticles exhibit the strongest magnetic response, as it would be easier to disperse them in solution and for them to pass through the porous media encountered in an oilfield situation.

Figure 5-8. 3D colormap surface for iron oxide nanoclusters. Summary of magnetic susceptibilities first iron oxide nanoclusters studied.
5.4.2. Enhanced magnetic susceptibility in iron clusters versus isolated particles

As previously mentioned, the magnetic susceptibilities in clusters are much larger than for isolated particles discussed in Chapter 4. This phenomenon is explained from the close interaction (exchange interaction) that exists in the individual primary particles that form the nanoclusters which increases the magnetization of the system. Whereas, isolated particles are typically coated with surfactants that prevent close interactions between each other neglecting exchange interactions. Therefore, the isolated particles develop a strong dipole-dipole interaction. A comparison between iron oxide nanoclusters (Figure 5-9A) and isolated nanocrystals (Figure 5-9B) was performed to confirm the much higher magnetic response of nanoclusters. Figure 5-9C shows that there is a significant difference between the magnetic susceptibility of both types of nanocrystals (both samples were analyzed in powder). This was promising in that further studies of nanoclusters could be executed such as the incorporation of other metals to boost the magnetic susceptibilities and an in depth investigation of the ideal cluster size and primary particle size of iron oxide nanoclusters.
Figure 5-9. Magnetic behavior of isolated iron oxide nanocrystals versus iron oxide nanoclusters.
TEM images of (A) iron oxide nanoclusters, (B) iron oxide isolated nanocrystals and (C) magnetization versus applied field of cluster nanocrystals and isolated nanocrystals.

5.4.3. Doping of other metals to the iron oxide crystal structure

The influence of the cluster composition on their magnetic susceptibility was further investigated. Figure 5-10A shows the hysteresis curve at room temperature for four different compositions of ferrite nanoclusters and all of the ferrites analyzed exhibit superparamagnetic behavior. Figure 5-10B shows the magnetic susceptibility curves and it can be observed that from the comparison of four different ferrites the one with the best magnetic behavior was MnZnFe$_2$O$_4$ with a magnetic susceptibility of 24.2.
Figure 5-10. Magnetic data of ferrite nanoclusters at room temperature. (A) Hysteresis curve at 300K and (B) magnetization versus applied field at 300K for ferrite nanoclusters. Samples analyzed in SQUID in powder. Approximately 5-8 mg of sample were used for the measurement.

Magnetic susceptibility at room temperature was measured for all ferrite nanoclusters previously described in this chapter. Table 5-3 summarizes all magnetic measurements performed on the ferrite nanoclusters. Based on the percentage of metal oxide, previously measured from TGA, the measured magnetic susceptibility of the samples was corrected. The highest susceptibility obtained for the ferrites was 24.2 for MnFe₂O₄ and the corrected value was 33.2.

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>Primary particle size (nm)</th>
<th>Cluster size (nm)</th>
<th>BET (m²/g)</th>
<th>TGA %MO</th>
<th>SQUID χ (SI) at 300K</th>
<th>SQUID corrected TGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn₀.₀₃Fe₂.₉₇O₄</td>
<td>5.2 ± 1.0</td>
<td>89 ± 11</td>
<td>121.8</td>
<td>77.5</td>
<td>10.9</td>
<td>14.1</td>
</tr>
<tr>
<td>Ferrite</td>
<td>Primary particle size (nm)</td>
<td>Cluster size (nm)</td>
<td>BET (m²/g)</td>
<td>TGA %MO</td>
<td>SQUID χ (SI) at 300K</td>
<td>SQUID corrected TGA</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------------</td>
<td>-------------------</td>
<td>------------</td>
<td>---------</td>
<td>----------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Mn$<em>{0.6}$Fe$</em>{2.4}$O$_4$</td>
<td>4.9 ± 5</td>
<td>139 ± 21</td>
<td>92.9</td>
<td>64.1</td>
<td>6.93</td>
<td>10.8</td>
</tr>
<tr>
<td>Mn$<em>{0.4}$Fe$</em>{2.6}$O$_4$</td>
<td>4.6 ± 1.1</td>
<td>126 ± 18</td>
<td>249.1</td>
<td>62.5</td>
<td>11.3</td>
<td>18.1</td>
</tr>
<tr>
<td>Mn$<em>{0.3}$Fe$</em>{2.7}$O$_4$</td>
<td>5.4 ± 1.1</td>
<td>64 ± 9.7</td>
<td>115.9</td>
<td>73.0</td>
<td>24.2</td>
<td>33.2</td>
</tr>
<tr>
<td>Mn$<em>{0.3}$Zn$</em>{0.7}$Fe$_{2.0}$O$_4$</td>
<td>5.6 ± 1.0</td>
<td>38 ± 7.1</td>
<td>116.5</td>
<td>73.4</td>
<td>23.7</td>
<td>32.3</td>
</tr>
<tr>
<td>Ni$<em>{0.04}$Fe$</em>{2.96}$O$_4$</td>
<td>6.1 ± 0.9</td>
<td>48 ± 7.7</td>
<td>164.2</td>
<td>74.7</td>
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<td>Ni$<em>{0.05}$Fe$</em>{2.95}$O$_4$</td>
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<td>45 ± 6.4</td>
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<td>81.7</td>
<td>17.8</td>
<td>21.8</td>
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<tr>
<td>Mn$<em>{0.4}$Zn$</em>{0.04}$Fe$_{2.6}$O$_4$</td>
<td>6.5 ± 1.1</td>
<td>54 ± 7.6</td>
<td>129.9</td>
<td>71.3</td>
<td>17.5</td>
<td>24.5</td>
</tr>
<tr>
<td>Mn$<em>{0.4}$Zn$</em>{0.04}$Fe$_{2.6}$O$_4$</td>
<td>5.9 ± 1.0</td>
<td>51 ± 8.4</td>
<td>154.7</td>
<td>72.2</td>
<td>24.0</td>
<td>33.2</td>
</tr>
<tr>
<td>Mn$<em>{0.4}$Zn$</em>{0.04}$Fe$_{2.6}$O$_4$</td>
<td>5.9 ± 1.1</td>
<td>37 ± 5.2</td>
<td>143.5</td>
<td>68.1</td>
<td>17.9</td>
<td>26.3</td>
</tr>
<tr>
<td>Mn$<em>{0.4}$Zn$</em>{0.04}$Fe$_{2.6}$O$_4$</td>
<td>5.4 ± 0.9</td>
<td>33 ± 5.1</td>
<td>135.5</td>
<td>70.4</td>
<td>19.7</td>
<td>28.0</td>
</tr>
<tr>
<td>Ni$<em>{0.01}$Zn$</em>{0.05}$Fe$_{2.94}$O$_4$</td>
<td>4.5 ± 0.8</td>
<td>84 ± 12</td>
<td>113.2</td>
<td>72.0</td>
<td>15.8</td>
<td>21.9</td>
</tr>
<tr>
<td>Mn$<em>{0.02}$Zn$</em>{0.05}$Fe$_{2.93}$O$_4$</td>
<td>4.8 ± 0.9</td>
<td>69 ± 10</td>
<td>107.9</td>
<td>75.3</td>
<td>18.6</td>
<td>24.7</td>
</tr>
<tr>
<td>Mn$<em>x$Fe$</em>{3-x}$O$_4$</td>
<td>5.5 ± 1.2</td>
<td>69 ± 11</td>
<td>106.4</td>
<td>82.3</td>
<td>17.0</td>
<td>20.7</td>
</tr>
<tr>
<td>Mn$<em>x$Fe$</em>{3-x}$O$_4$</td>
<td>6.2 ± 1.1</td>
<td>83 ± 12</td>
<td>107.6</td>
<td>79.9</td>
<td>17.7</td>
<td>22.2</td>
</tr>
<tr>
<td>Mn$_x$Zn$<em>y$Fe$</em>{3-x-y}$O$_4$</td>
<td>6.0 ± 1.0</td>
<td>49 ± 7.2</td>
<td>94.6</td>
<td>78.4</td>
<td>23.1</td>
<td>29.4</td>
</tr>
<tr>
<td>Mn$_x$Zn$<em>y$Fe$</em>{3-x-y}$O$_4$</td>
<td>5.6 ± 0.9</td>
<td>47 ± 8.1</td>
<td>131.9</td>
<td>77.9</td>
<td>16.8</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Table 5-3. Summary of magnetic susceptibilities of ferrite nanoclusters.
Table summarizes cluster size, primary size of ferrite nanoclusters. Magnetic susceptibilities measured from SQUID have been corrected using the total metal oxide measured.
5.4.4. Cluster size and primary particle size dependence

The previously described data supports the fact that cluster size and primary nanoparticle size are crucial parameters, accordingly an in depth study of the effect on the magnetic properties of cluster size and primary particle size was performed to find the ideal size of both cluster size and primary particle size that would have the highest magnetic response. From previous studies, it was discovered that the smaller cluster size the higher the magnetic susceptibility. Therefore, cluster size with ranges from 90 to 25 nm and primary particle size from 10.5 to 5.5 nm were investigated. Figure 5-11 shows the collection of all samples analyzed and it is observed that the highest susceptibility obtained for iron oxide nanocluster was 24.5 for clusters of around 50 nm with a primary particle size of 6.5 nm. This was promising because it would be possible to make clusters stable in solution without sacrificing the enhanced magnetic properties of the nanoclusters.
Figure 5.11. 3D colormap surface of iron oxide nanoclusters. Data summarizes the magnetic susceptibilities of all iron oxide nanoclusters synthesized using solvothermal method.

5.4.5. Concentration dependence of iron oxide clusters in solid and liquid environments

It is of great relevance to know the susceptibility at different volume percent concentrations in order to apply these in real world conditions. Therefore, a dilution study was performed on the nanocluster powders to study the dependence of the magnetic susceptibility on the percentage of clusters. Potassium chloride (KCl) was used a magnetically inert powder to make the dilutions on the solid state. The iron oxide nanocluster used had a 57 nm cluster size and a 5.9 nm primary particle size. The nanocrystal clusters were diluted to a desired weight percentage.
using KCl and their magnetic susceptibility was analyzed using SQUID. The weight percentage measured was then converted to volume percent using KCl and magnetite densities which are 1.984 g/mL and 5.15 g/mL respectively. Figure 5-12 shows the magnetic susceptibility as a function of concentration of the iron oxide nanocluster. These data confirms a linear relationship between the magnetic susceptibility of the nanoclusters and their volume percentage.

![Graph showing magnetic susceptibility versus volume percentage](image)

**Figure 5-12. Volume percent versus magnetic susceptibility of iron oxide nanoclusters.**
Dilution study of iron oxide nanoclusters in KCl. Data was analyzed in powders and collected in SQUID.

Additionally, colloidal stability of the iron oxide nanoclusters is an important achievement for their characterization and application. Colloidally stable nanoclusters have been successfully synthesized by controlling the cluster size,
porosity and surface chemistry of the cluster (Figure 5-13A). The iron oxide clusters were successfully synthesized using PAA as the polymeric stabilizing agent. Figure 5-13B shows a TEM image of the colloidal solution of iron nanoclusters. From TEM cluster size was 24.4 nm and primary particle size had a size of 5.8 nm. Figure 5-13C shows a stability study that was performed with DLS for the iron clusters. Initially, the iron oxide nanoclusters were analyzed in DLS every day for a week. Since, it was observed that they were stable over the whole period, they were then measured again every week until a month was completed. Data shows that the colloidal nanoparticles are stable over the month that they were analyzed since there is no significant change in the hydrodynamic diameter of the nanoclusters over the period they were analyzed.
Figure 5-13. Ferrite nanoclusters dispersed in water.

(A) Stability study of iron oxide nanoclusters with DLS, (B) Iron oxide nanoclusters dispersed in water and (C) TEM image of iron oxide nanoclusters analyzed in DLS. Nanoclusters were coated with PAA.

Also, a dilution study of iron oxide nanoclusters in water was performed to study the dependence of the magnetic susceptibility on the percentage of clusters in water. Magnetic susceptibility data was collected in VSM. Figure 5-14 shows the magnetic susceptibility of a colloidal stable sample at different volume percentage in water. The sample iron oxide nanocluster was concentrated using spin filter technique to a final concentration of 1.4v%. An important discovery was that the clusters remained stable at this high concentration. Five different dilutions were performed down to a concentration of 0.4v%. Magnetic susceptibility was collected for each concentration where the data again confirmed that there is a linear
relationship between the magnetic susceptibility of the nanocrystal clusters and their volume percentage in water.

![Graph showing relationship between volume percent and relative susceptibility.](image)

**Figure 5-14. Volume percent versus relative susceptibility of iron oxide nanocluster.**

Sample initial concentration was 1.4 v%. Cluster size was 24.3 nm and primary size 5.8 nm. Data was collected in VSM.

### 5.5. Conclusions

In essence, the successful synthesis of ferrite nanocluster, the high magnetic susceptibilities observed in the nanoclusters and the colloidal stability of nanoclusters were the main topics addressed in this chapter. The magnetic data collected for nanoclusters confirmed that higher magnetization is obtained due to
the type of interparticle interactions (exchange interactions) present in the particles.

The cluster size and primary size of iron oxide nanocluster were optimized to find the ideal size of each parameter that would have the highest magnetic response. It was found that for iron oxide that the ideal cluster size and primary particle size should be around 50 and 6.5 nm respectively. The highest magnetic susceptibility found for iron oxide nanoclusters was 24.4.

The doping of iron oxide nanoclusters with other metals (M^{2+}) was performed to identify their impact on the magnetic susceptibility since it is known that ferrites have very large susceptibilities. Varied ferrite nanoclusters were successfully synthesized and the highest magnetic susceptibility obtained was 24.2 which corresponded to a manganese ferrite (Mn_{0.3}Fe_{2.7}O_{4}). The cluster size and primary particle size were 64 and 5.4 nm respectively. The highest magnetic susceptibilities for iron oxide and manganese ferrite are very similar, but in the case of manganese ferrite there is still the possibility of the optimization of composition as well as size to increase much higher the magnetic susceptibility.

Finally, efforts were completed to ensure the nanoclusters stable in water. The nanoclusters were successfully coated with PAA and stability was studied over a period of one month where results show that they remained stable having no significant change in the hydrodynamic diameter which was measured with DLS. With the stable clusters in water, a dilution study was performed to observe the relationship between the magnetic susceptibility versus concentration of
nanoclusters. It was found via both SQUID and VSM measurements that they have linear relationship which is ideal to understand the amount of material required for a desired magnetic response. These synthesized and characterized ferrite nanoclusters are very promising materials due to the enhanced magnetic properties they exhibit.
Chapter 6

Applications of magnetic oxide nanocrystals

6.1. Introduction

As we have discussed in previous chapters, magnetic nanoparticles have many useful applications due to their beneficial and versatile properties. In this chapter three different applications of magnetic nanoparticles will be discussed: magnetic nanoparticles for down-hole imaging, MRI relaxation, magnetic nanoparticles in separation techniques.

6.2. Magnetic nanoparticles for down-hole imaging

This section discusses the potential of magnetic nanoparticles use for down-hole imaging in the oil and gas industry. Magnetic nanoparticles have recently garnered much attention in key such as production, drilling, enhanced oil recovery,
exploration and refining. According to the U.S. Department of Energy (DOE) approximately 67% of the oil remains undiscovered. Therefore, exploration of unconventional reservoirs is imperative.\textsuperscript{119} However, conventional technologies are not equipped to collect underground oil. Magnetic nanoparticles may have the potential to solve key technical challenges associated with operating in deep water or under harsh conditions. Specifically, due to their significant magnetic properties, magnetic nanoparticles can be used to accurately locate and characterize hydrocarbons.

Magnetic nanoparticles are already been used in the medical field for imaging.\textsuperscript{120,121} These same nanoparticles could also potentially be used in the oil and gas industry to exploit current technologies that are employed for reservoir characterization such as seismic and electromagnetic measurements. The current techniques used for reservoir characterization lack of depth of investigation or image resolution. For example, seismic surveys produce low-resolution images and are more sensitive to rocks rather than fluids. Consequently, more sensitive surveys are needed to enable investigating farther into a reservoir and to generate higher resolution images.

Cross-well electromagnetic induction is a survey method that explores areas between wells, provides higher depth of investigation, and is sensitive to fluids.\textsuperscript{122,123} Data are collected by lowering a series of receivers into a wellbore, which remain stationary, and then lowering an EM transmitter into another wellbore several meters apart. The distance between the wellbores depends on
their specific conditions, such as the casing characteristics. Typically, in an open-hole wellbore, the distance between transmitter and receiver can be up to 1000 m. The EM transmitter produces magnetic fields at frequencies between 5 Hz and 1 kHz. The EM transmitter moves up and down in the well transmitting signals down-hole. EM transmitter generates a magnetic field, known as the primary field, which induces a current in conductive formations. This current produces an opposing secondary electromagnetic field. The receivers in the opposite wellbore detect the signals from the primary magnetic field generated by the transmitter and the induced secondary magnetic fields.\textsuperscript{124}

Magnetic nanoparticles are intended to be used for down-hole imaging via the cross well electromagnetic concept (Figure 6-1). As part of this process, magnetic nanoparticles would be injected with the injection fluids used for waterflooding which is used to increase pressure in order to stimulate the production of the reservoirs. The EM transmitter generates magnetic fields which induce secondary magnetic fields as they encounter magnetic nanoparticles. Both primary and secondary magnetic fields will therefore be detected by the series of receivers in the opposite wellbore.
Figure 6-1. Magnetic nanoparticles in waterflooding applications. Magnetic nanoparticles are injected through the injection well. Signals from the magnetic nanoparticles are collected in the production well by a series of receivers and transferred to an amplifier where an image is then collected.

The signal detected by the receivers is the magnetic dipole radial field (Equation 6-1), where $k$ is a wave vector, $m$ is the magnetic moment of the nanoparticle, $\mu$ is the relative permeability, $\omega$ is the angular frequency, $\varepsilon$ is the permittivity and $\sigma$ is the dielectric conductivity.

$$H_z = \left(\frac{m}{4\pi r^3}\right)(1 - ikr - k^2 r^2)e^{ikr}$$

$$k = \sqrt{i\mu\mu_0\sigma\omega + \mu\mu_0\varepsilon\varepsilon_0\omega^2}$$

Equation 6-1. Magnetic dipole radial field
In order to increase the magnetic dipole radial field, the magnetic permeability of magnetic materials was enhanced. Magnetic permeability is related to magnetic susceptibility.

\[ \chi_v = \mu_v - 1 \]

**Equation 6-2. Magnetic susceptibility**

Magnetic susceptibility was measured for magnetic nanoparticles at low fields to simulate reservoir conditions.

### 6.2.1. Screening tools for magnetic nanoparticles

A key outcome of this study was to determine a method to screen the magnetic materials available and define the requirements for a material to serve as a nanomagnetic contrast agent for down-hole applications. Magnetic characterization is typically performed using SQUID and VSM. Both instruments are capable of collecting any types of DC data (magnetization, hysteresis, and initial magnetic susceptibility). The two main differences between these instruments are that higher magnetic fields (up to 7 T) can be applied in SQUID, and the analysis of samples using SQUID takes much longer. However, in VSM highest magnetic field that can be applied is 3 T and the collection time required for measurement is extremely short. In addition, SQUID has the capability of collecting AC data (frequency dependent) from 0.1 to 1000 Hz.
Given their unique characteristics and the fact that both instruments can measure magnetic susceptibilities, SQUID and VSM were chosen as a screening tool for this study. One of the advantages of using these instruments is that not a lot of material is needed for analysis. Both required approximately 40 μL of solution for liquid samples and around 3-5 mg of powder sample for magnetic analysis. Magnetic susceptibilities for ferrite nanocrystals measured at room temperature in both instruments were analyzed for comparison (Figure 6-2). It was observed that magnetic susceptibilities measured by both instruments show the same trend: zinc ferrite has the highest magnetic susceptibility, followed by 10 nm and 8 nm manganese ferrite. However, magnetic susceptibility measured by SQUID shows a 15% higher value than in VSM.

**Figure 6-2. Magnetization versus applied field of ferrite nanocrystals.**
Ferrite nanocrystal solutions measured in (A) SQUID and (B) VSM at a concentration of 1.0% by volume in kerosene.
Despite the similarity in trends observed, using both instruments to measure initial magnetic susceptibility is a novel approach that enabled us to draw a comparison between magnetic data collected by SQUID and VSM and the standards methods used in the literature. Another somewhat rudimentary technique to measure magnetic susceptibility was used in collaboration with researchers at the University of Texas at Austin (UT Austin; Figure 6-3). Magnetic measurement with this technique provides a more reliable value for the real magnetic susceptibility of the samples since that value is used for the real application of down-hole imaging. The setup required significant sample volumes (30 mL) at high concentrations (0.5-2% by volume). The setup consisted of a direct-coupled amplifier, a lock-in amplifier, a magnetic sensor, and copper wire to form the solenoid that would produce the current.
Figure 6.3. Rudimentary setup to measure magnetic susceptibility.
The measurement requires a DC amplifier, a Lock-in amplifier, copper wire to form a solenoid, a teflon piece to hold the ping pong ball (sample holder) and a magnetic sensor.

Hollow plastic spheres (ping pong balls) were filled with approximately 30 ml of the liquid samples. The spheres were placed in a uniform magnetic field created by an air-filled solenoid operating at a frequency of 3 Hz. The perturbation of the magnetic flux $\Delta B$ along the axis of the solenoid was then measured by a sensor. Due to the fact that the sample is spherical, the effect of demagnetization on the measured field perturbation is known exactly and can be accounted for. The susceptibility of the sample is given by Equation 6-3 where $z$ is the distance between the sample and the sensor, $V$ is the sample volume, and $\Delta B$ is the normalized dimensionless change in the magnetic flux density.
\[ \chi = \frac{6\pi z^3 \Delta B}{3V - 2\pi z^3 \Delta B} \]

Equation 6-3. Magnetic susceptibility

First, the magnetic susceptibility of a commercial sample from Ferrotec (EFH1) was investigated using both SQUID and the UT Austin technique. The concentration of EFH1 was 8.7% by volume, measured using ICP-OES. In SQUID, the typical magnetization curve was measured from 0 to 50 Oe to simulate fields that will be applied down-hole (Figure 6-4). It was observed that the magnetic susceptibility for the commercial sample was 1.22.

![Magnetization curve](image)

**Figure 6-4. Magnetization versus applied field of commercial sample.**
Magnetic susceptibility of commercial sample from Ferrotec EFH1. Photograph of the commercial sample.
One important factor to consider when measuring magnetization is the demagnetization field (Figure 6-5A). This is the magnetic field produced by the magnetization of magnetic materials which reduces the total magnetic moment. Surface poles form at the ends of a magnetized material and create a demagnetization field that is in the opposite direction of the magnetization. The demagnetization field reduces the magnetic field applied. The strength of the demagnetization field depends highly on the geometry of the material analyzed. If it is spherical, the material will become magnetized to the same extent in all directions. However, if it is a non-spherical shape, it will be easier to magnetize the long axis than the short axis since the short axis requires stronger magnetic fields to generate the same magnetization. Given this difference, a demagnetization factor that depends on the shape of the material was used to calculate total magnetization of magnetic materials taking into account the demagnetization field (Figure 6-5B).

![Figure 6-5](image)

**Figure 6-5.** (A) Demagnetization field effect on magnetic materials and (B) demagnetization factor for varied geometries.
The real magnetic susceptibility can be calculated using the demagnetization factor of the geometry of the material and the magnetic susceptibility experimentally measured by SQUID or VSM (Equation 6-4).

\[ \chi = \frac{1}{\left(\frac{1}{\chi_a} - D\right)} \]

**Equation 6-4. Real magnetic susceptibility**

The magnetic susceptibility of EFH1 measured by SQUID was 1.22. Taking into account the demagnetization factor of a sphere, the magnetic susceptibility was corrected to 2.05. Magnetic susceptibility was also measured using the UT rudimentary technique and it was found to be 2.26 ± 0.2. The discrepancy between the two measurements was less than 10% which is not very significant. Based on these results, the magnetic susceptibilities that were analyzed in SQUID are expected to be somewhat higher.

Once the differences between measuring magnetic susceptibility with different techniques were investigated on commercial samples, a dilution study of iron oxide nanoclusters in solutions was performed. Iron oxide nanoclusters were the samples chosen for the present research because they exhibited large magnetic susceptibilities in previous studies. An iron oxide nanocluster solution was concentrated to 0.5% by volume and diluted to 0.25% and 0.125% by volume. Magnetic susceptibility was collected for three different concentrations (Figure 6-6). It was observed that the three points follow a linear fit which is ideal since the
value of magnetic susceptibility at a desired concentration can be calculated. Therefore, the normalized value at 2% by volume comes up to 3.48, which is much higher than any commercially available nanoparticles.

![Graph](image)

**Figure 6-6. Magnetic susceptibility versus volume percent concentration of iron oxide nanoclusters.**

Linear behavior is observed for iron oxide nanoclusters coated with PAA at concentration of 0.5%, 0.25% and 0.125% by volume.

The magnetic susceptibilities measured for the iron oxide nanoclusters are high enough to produce an image of a reservoir of interest. Collaborators performed studies with an iron oxide sample at a concentration of 0.1% by volume with a magnetic susceptibility of 0.3. They were able to generate an image with the sample and concentration of iron oxide used. While the ideal scenario is to have the highest magnetic susceptibility as possible, it is important to be aware that problems with density contrast could arise at high concentrations.
6.2.2. Conclusions

Extant research has demonstrated that magnetic nanoparticles can be used to exploit current oil recovery techniques such as waterflooding and hydraulic fracturing. However, these techniques suffer from an inability to accurately determine locations of water front or fracturing down-hole. Seismic and well logs technologies are the two primary methods used to characterize a reservoir but they lack of depth of investigation or the images gathered have a very low resolution. Therefore, one method to yield accurate, reliable information regarding a conventional reservoir is the application of magnetic material. These materials could be injected with injection or fracturing fluids and their location could be then determined by electromagnetic signals using the crosswell technique.

Several magnetic nanoparticles were screened using SQUID and VSM, which are magnetic characterization instruments. Magnetic data from both instruments was compared and it was found that SQUID shows moderately higher magnetic susceptibility values. In addition, the magnetic susceptibility of magnetic particles was measured using a conventional bench scale setup. The only disadvantage of this technique was that it required a lot of material. However, this technique yielded more accurate measurements, since the measurement was already corrected for any demagnetization field.

First, calibration measurements were performed with a commercial iron oxide sample. A 10% difference was found in the magnetic susceptibility between SQUID measurement and the bench scale setup. A dilution study of one of the most
A promising iron oxide nanocluster solution was then performed. The magnetic susceptibilities measured using the bench scale setup gave values high enough to generate an image. Previous measurements performed for imaging applications used an iron oxide sample that had a magnetic susceptibility of 0.3 at a concentration of 0.1% by volume. The magnetic susceptibility of our lab-synthesized sample was almost two times higher than the used sample for imaging studies. Based on our results, the samples that have been presented in this chapter could have great potential for down-hole imaging given the high magnetic susceptibilities observed.

6.3. $R_2$ relaxation dynamics for ferrite nanocrystals

The second application of ferrite nanocrystals explored in this chapter was MRI relaxation. Magnetic resonance imaging has become one of the most powerful diagnostic tools in medicine because of its non-invasive nature; however one of the major problems associated with this technique is its low signal sensitivity.\(^{126}\) The use of contrast agents enhances the MR signal by increasing the contrast between normal and diseased tissue.\(^{127}\) The MRI signal is recognized by the excitation of magnetic moments when a radio frequency is applied and is determined by the imaging sequence.\(^{65}\) The MRI sequence weights the effect of the net magnetization of hydrogen protons and relaxation mechanisms. There are two types of relaxation mechanisms: longitudinal relaxation ($T_1$) which is also known as spin-lattice
relaxation time and the transverse relaxation ($T_2$) which is also referred to as spin-spin relaxation. Moreover, the effective transverse relaxation, $T_2^*$, symbolizes the increase in relaxation produced by inhomogeneities on the magnetic field. Thus, $T_2^*$ can have a much smaller signal than $T_2$ and would result in signal loss which produces a negative contrast. This mechanism can be assessed in the concentration-independent transverse relaxivities $r_2$ and $r_2^*$.

Superparamagnetic iron oxide nanocrystals used as contrast agents enhance the tissue contrast by increasing the relaxation rate of water in the area of interest. These nanocrystals have the greatest effect on the $T_2$ relaxation rate due to their large magnetic moment.$^{128}$ $T_2$ contrast agents generate dark or negative contrast images and are known as $T_2$ negative agents.$^{129}$ The MRI enhancement is directly linked to the saturation magnetization of the nanoparticles. Several studies have shown that the MRI enhancement of magnetic nanoparticles is dependent on size, composition, surface properties and degree of aggregation.$^{130}$

The composition of magnetic nanocrystals can have a great impact in the MR signal enhancement.$^{131}$ The MR can be increased by incorporating of other metals into the crystal structure of iron oxide.$^{130}$ Several approaches using varying compositions have been pursued to attain high and tunable nanomagnetism. Cheon et al, demonstrated an increase in the MR signal when iron oxide is doped with Mn$^{2+}$ ions and is significantly higher than conventional iron oxide nanoparticles.$^{126}$ The doping of Zn$^{2+}$ has also been found to greatly increase the signal since it causes redistribution of cations between tetrahedral and octahedral sites. For example,
when Zn\textsuperscript{2+} ions are added, they occupy tetrahedral sites and produce a reduction of the antiferromagnetic coupling of Fe\textsuperscript{3+} ions in the tetrahedral and octahedral sites.\textsuperscript{131} It is important to note that, although MRI signal enhancement is vital, it has been found that lowered doses of contrast agents can be administered while still maintaining a good MR signal.

The effect of size on MRI contrast has been thoroughly studied.\textsuperscript{132,48} There are three different regimes in which magnetic nanoparticles could fall in: the motional average regime (MAR), the static dephasing regime (SDR) and the echo-limiting regime (ELR).\textsuperscript{133} As size increases, the \( r_2 \) increases in the MAR regime until it reaches a maximum plateau in the SDR regime. Further increase in size results in a decrease of \( r_2 \) relaxivity (ELR). Despite that the highest \( r_2 \) relaxivity values are observed in the SDR regime, the magnetic nanoparticles that are used for MRI contrast agents applications fall into the MAR regime since in the SDR regime nanoparticles can suffer of aggregation due to strong dipolar interactions.\textsuperscript{134} Previous studies have demonstrated that as size increases, saturation magnetization increases, and high relaxivities are therefore observed.\textsuperscript{135,83}

In addition, extant studies have revealed that aggregating single isolated magnetic nanoparticles can enhance magnetic properties.\textsuperscript{136} These aggregated particles are of great interest for MRI since it enhances the contrast signal.\textsuperscript{137,138,139} Gao et al. presented a study of superparamagnetic polymeric micelles, which revealed that they had a much higher \( r_2 \) relaxivity than single iron oxide particles.\textsuperscript{138}
Composition, size and aggregation effect on $r_2$ relaxivity for MRI studies will be discussed in the following sections.

6.3.1. MR relaxivity measurements

To perform the MR relaxivity measurement, magnetic nanoparticles in organic solution were phase transferred using PAMPS-LA. Details of phase transfer have been discussed in Chapter 2. Different concentrations of magnetic nanocrystals were prepared by dilution of the stock solution coated with PAMPS-LA. To measure $r_2$ of ferrite nanocrystals, a MR relaxometer (NMR analyzer, mq 60, Bruker) was used at 1.41 T. The relaxivity values, $r_2$, were calculated from the slope between $1/T_2$ and of magnetic nanocrystals concentration.

6.3.2. MR relaxation dynamics

6.3.2.1. Composition effect on MRI contrast

For this experiments, the relaxivity values ($r_2$) of various ferrite nanocrystals were explored from the slope in a plot of $1/T_2$ and metal concentrations. First, varied compositions were investigated: magnetite, cobalt zinc ferrite and manganese zinc ferrite (Figure 6-7). The largest $r_2$ value obtained was 285 mM$^{-1}$s$^{-1}$ for manganese zinc ferrite. This result confirmed that the doping of zinc ions to the iron oxide structure boosts the magnetization resulting in higher $r_2$ relaxivity. The second highest relaxivity attained was 232 mM$^{-1}$s$^{-1}$ for cobalt zinc ferrite. The lowest $r_2$ relaxivity was 158 mM$^{-1}$s$^{-1}$ for magnetite.
This composition dependent experiment showed that composition plays a major role in the magnetic properties of the nanoparticles and can significantly affect their contrast enhancing capabilities. The relaxivities obtained for ferrite nanocrystals in this experiment were much higher than for the conventional iron oxide particles Ferridex ($r_2$ value of 110 mM$^{-1}$s$^{-1}$) and cross-linked (CLIO is 62 mM$^{-1}$s$^{-1}$).

![Graph showing 1/T2 (s$^{-1}$) vs. Fe Concentration (mM) for different nanoparticles: Fe$_3$O$_4$, MnZnFe$_2$O$_4$, and CoZnFe$_2$O$_4$.](image)

Figure 6-7. Plots of ferrite nanocrystals $r_2$ values dependent on composition. Plots of $r_2$ values depending on their composition for magnetite, manganese zinc ferrite and cobalt zinc ferrite nanocrystals.

### 6.3.2.2. Size effect on MRI contrast

The next experiments involved investigating the size effect. The size effect on MRI contrast has been extensively studied in iron oxide nanoparticles.\textsuperscript{140,141} Many research studies investigating iron oxide have shown that as size increases,
the $r_2$ value increases. However, according to SDR theory, a plateau is reached once the size increases to 50 nm or more. Size dependent experiments were therefore performed on ternary ferrite nanocrystals to observe the effect on $r_2$ relaxivity. The primary interest of using ternary ferrites stemmed from their highly magnetic properties due to the doping of metal cations. As of the date of writing, there was no research reported involving size dependence studies of ternary ferrites.

To complete these experiments, three different sizes of manganese zinc ferrite (10, 14 and 16 nm) were synthesized (Figure 6-8A). Relaxivity data were collected for each size. It was observed that as the size of the nanoparticle increased, the $r_2$ relaxivity increased. For manganese zinc composition, there is still room to continue increasing the size of nanoparticles and observe whether the $r_2$ relaxivity continues to increase.

A size dependent experiment was also performed on cobalt zinc ferrite. Sizes from 10 to 29 nm were studied, and it was observed that as size increases $r_2$ relaxivity decreases (Figure 6-8B). Cobalt zinc ferrite does not follow the typical behavior of iron oxide nanoparticles where relaxivity increases as size increases. Size dependent studies for each composition analyzed would be ideal to find the best magnetic nanoparticle that exhibits the highest $r_2$ relaxivity.
Figure 6-8. Plots of $r_2$ relaxation of ferrite nanocrystals versus total metal concentration.
Plots of $r_2$ depending on size of (A) manganese zinc ferrite and (B) cobalt zinc ferrite nanocrystals.

6.3.2.3. Aggregation effect on MRI contrast

Finally, the aggregating effect on MRI contrast was investigated. Aggregating small single magnetic nanoparticles can increase the magnetic properties of nanoparticles. Many studies have demonstrated that the development of nanoclusters causes a dramatic increase in $r_2$ relaxivity. Iron oxide, manganese and manganese zinc ferrite nanoclusters were synthesized and studied for $r_2$ relaxivity. Figure 6-9 shows TEM images of ferrite nanoclusters. Iron oxide nanoclusters had a cluster size of $24.4 \pm 2.9$ nm and a primary particle size of $5.8 \pm 1.0$ nm. Manganese ferrite had a cluster size of $39.8 \pm 4.1$ nm and a primary size of $5.4 \pm 0.8$ nm. Manganese zinc ferrite cluster size was $41.2 \pm 4.7$ nm with a primary particle size of $5.2 \pm 0.7$ nm. The ferrite nanoclusters are polyacrylic acid (PAA)-coated.
Figure 6-9. TEM images of ferrite nanoclusters.
TEM images ferrite nanoclusters (A) Fe₃O₄, (B) Mn₀.₃Fe₂.₇O₄, and (C) MnₐZn₀.₁Fe₂.₈O₄ coated with PAA.

The relaxivity values of ferrite nanoclusters were determined from the slope in a plot $1/T_2$ and iron concentration (Figure 6-10). The $r_2$ relaxivity values were 696, 510, and 396 mM⁻¹s⁻¹ for manganese zinc ferrite, manganese and iron oxide nanoclusters, respectively. $R_2$ relaxivities are much higher than relaxivity values for isolated nanoparticles.
Figure 6-10. Plot of the linear correlations of transverse relaxation rates of ferrite nanoclusters against iron concentration (mmol/L).

Plots of $r_2$ of iron oxide, manganese ferrite, and manganese zinc ferrite nanoclusters.

6.3.3. Conclusions

The size, composition, and aggregation effect of magnetic nanoparticles on MR relaxivity values were studied. These $r_2$ relaxivity experiments with varied compositions of isolated nanocrystals showed that MR contrast signal can be enhanced by the substitution of other metal cations instead of Fe$^{2+}$. In addition, the doping of zinc ions into the iron oxide showed an enhancement in the $r_2$ relaxivity values.

A size dependent experiment was conducted with manganese zinc and cobalt zinc ferrite nanocrystals. The $r_2$ relaxivity value for cobalt zinc ferrite
nanocrystal was highest for the smallest size. In contrast, the \( r_2 \) relaxivity values for varied sizes of manganese zinc ferrite showed that the highest value corresponded to the largest size. For this composition, the \( r_2 \) relaxivity could be increased further as the size of the nanocrystal increase.

Finally, ferrite nanoclusters were studied for \( r_2 \) relaxivity. The \( r_2 \) values measured were significantly higher than the relaxivity values for single isolated nanoparticles. This is due to the increase in the effective magnetic size when single particles are aggregated. The size, compositions, and degree of aggregation of ferrite nanocrystals can be extremely valuable for MR contrast since these nanocrystals exhibit high \( r_2 \) relaxivity values. The \( r_2 \) relaxivity values for all nanocrystals investigated in this study have a much higher \( r_2 \) relaxivities than the commercial contrast agents currently on the market.

6.4. Magnetic separation

Magnetic nanoparticles are widely used in applications such as MR imaging, drug delivery and environmental remediation.\textsuperscript{49,67,30} The main characteristics of interest for each of these applications is the magnetic properties that these nanoparticles exhibit. For example, it is possible to concentrate or collect magnetic nanoparticles even at small magnetic fields.\textsuperscript{66} The magnetic separation method has been successfully used for water purification and magnetic drug targeting that results in the release of nanoparticles and their cargo to a specific site.\textsuperscript{142,143}
The major problem associated with drug administration is the current inability to target a specific location in the body. Large doses are used to target a specific organ or disease site which can have toxic effects on non-target organs. Magnetic separation could therefore be used to target specific sites, thus reducing the use of excess drugs and minimizing their side effects while simultaneously increasing the concentration of the drugs at the target sites.

Magnetic separation is a technique that is based on a competition between varied forces. When a mixture is fed into a separator in the presence of an applied field, magnetic forces pull magnetic nanoparticles and frictional, gravitational and inertial forces pull other particles. As a result, magnetic nanoparticles are separated from non-magnetic nanoparticles. In this study, magnetic separation of nanocrystals was performed on a Frantz Canister model L-1CN High Gradient Magnetic Separator (HGMS; Figure 6-11), equipped with a stainless steel column packed with stainless steel wool (diameter~50 μm) placed between two poles of an electromagnet producing magnetic fields from 0 to 1.6 T. When a magnetic field is applied during this process, the stainless steel wool dehomogenizes the magnetic field resulting in large field gradients around the wool that attract and trap magnetic particles and trap them. The attraction of nanoparticles highly depends on the generation of the large magnetic field gradients as well as the size and magnetic properties of nanoparticles which is given by Equation 6-5 where $\mu_0$ is the permeability of free space, $V_p$ is the volume of the particle, $M_p$ is the magnetization of the particle and $H$ is the magnetic field applied:
\[ F_m = \mu_0 V_p M_p \cdot \nabla H \]

**Equation 6-5. Magnetic force on a nanoparticle**

While High gradient magnetic separators (HGMS) have been already been used for the separation of large complexes in the sub-micron range in protein and environmental separation processes, the study of isolated magnetic nanoparticles has been discussed in much less depth.\textsuperscript{147,148} Colvin et al. reported the successful separation of a multiplex sample of iron oxide nanocrystals by varying the strengths of the magnetic field.\textsuperscript{149} Inspired by this research, we performed a composition dependent experiment on ferrite nanocrystals to observe whether it was possible to separate magnetic materials depending on their composition.

**Figure 6-11. High gradient magnetic separator.**
6.4.1. Magnetic separation of ferrite nanocrystals

The last application investigated in this study was magnetic separation. Ferrite nanocrystals of different compositions at a fixed size were studied to determine the ideal conditions for multiplex magnetic separation. Nanocrystals were synthesized to a fixed size (10 nm) via thermal decomposition of metal oleates. Magnetite nanocrystals were produced from the mixture of 1 mmol iron oleate and 3 mmol oleic acid in 10 g of 1-ODE. Manganese ferrite was prepared by combining 1 mmol of iron oleate and 0.5 mmol of manganese oleate with 3 mmol of oleic acid in 10 g of 1-ODE. Cobalt ferrite was prepared by reacting 1 mmol of iron oleate and 0.5 mmol of cobalt oleate with 3 mmol of oleic acid in 15 g of 1-ODE. Lastly, zinc ferrite was synthesized by thermal decomposition of 1 mmol of iron-zinc oleate complex (1:5) with 3 mmol of oleic acid in 10 g of 1-ODE. The reactions were kept at 315°C for 2 h except for magnetite which was only heated for 1 h. Figure 6-12 shows TEM images of monodisperse ferrite nanocrystals with average diameters of 10.7 ± 1.0, 10.4 ± 0.9, 10.4 ± 1.1 and 10.4 ± 0.9 nm.
Figure 6-12. TEM images of ferrite nanocrystals at a fixed size.
TEM images of ferrite nanocrystals (A) Fe₃O₄, (B) MnFe₂O₄, (C) CoFe₂O₄ and (D) ZnFe₂O₄.

6.4.2. Batch magnetic separations

To assess whether magnetic separation was feasible for each composition ferrite nanocrystals of varied compositions were fed through the HGMS column and various magnetic fields ranging from 0 to 1.5 T. First, a control experiment was performed by passing a solution of magnetic nanocrystals with no applied field, and it was further analyzed if magnetic nanocrystals were retained in the column. Then, each ferrite nanocrystal solution in hexane was passed through the column, collected and analyzed to observe the percent retention of nanoparticles in the column at different magnetic fields (Figure 6-13). Individual analysis of each ferrite
nanocrystal was then performed to observe the fields at which multiplex separation would be possible.

**Figure 6-13. Schematic of HGMS experimental setup.**
The magnetic field is adjusted through the power supply. The ferrite nanocrystal solution is passed through a packed column with stainless steel wool. The effluent solution is collected.

Since one of the goals of this study was to separate varied ferrite nanocrystals, it was important to conduct a concentration experiment to determine whether concentration would affect the magnetic separation experiments. A magnetite sample was chosen as a model for this experiment. Concentrations were calculated based on nanoparticle molarity to ensure that they each contained the same number of particles independent of size or composition. Four different concentrations were analyzed, 50 nM, 100 nM, 150 nM, and 250 nM (Figure 6-14). The results from the concentration experiment reveal that there is a significant difference for the smallest concentration tested (50 nM) which showed much lower
retention percentages than higher concentrations. Higher concentrations of 100, 150, and 250 nM showed similar retention rates. Therefore, ferrite nanocrystals experiments were performed at a concentration of 100 nM since there was no need to use much higher concentrations.

Figure 6-14. Concentration dependence experiment of magnetic separation. Four different concentrations of iron oxide nanocrystals were tested to determine the ideal concentration for magnetic separation of ferrite nanocrystals.

For the first experiment, a volume of 10 mL at a concentration of 100 nM of nanoparticles was passed through the column at different magnetic strengths. The column was washed three times with 10 mL of hexane to remove nanoparticles retained in the column. The magnetic fields applied for analysis were 0.01, 0.02, 0.04, 0.08, 0.12, 0.24, 0.5, 0.7 and 1 T. Before passing the solution through the
column, the magnetic field was set for 10 min at the desired field for field stabilization. No higher fields were needed since all samples had reached magnetic saturation at 1 T.

For most applications it is also crucial to observe the magnetic behavior of nanoparticles at low magnetic fields. Quantitative analysis of metal content of the starting suspensions and the effluent enabled for the calculation of the percent retention of nanoparticles at different applied magnetic fields. This analysis showed that magnetite and zinc ferrite maintained nearly complete retention at 1 T with 99% and 97% retained, respectively (Figure 6-15). Given that these two compositions have a similar retention, it would be difficult to magnetically separate them. Manganese ferrite and cobalt ferrite are the nanoparticles that show the lowest percent retention compared to other nanoparticles. The greatest difference in the percent retention was at low fields. While there is already 80% retention of nanoparticles at 0.045 T, for manganese ferrite there is only 50% retention. Therefore, manganese ferrite and magnetite nanocrystals were chosen in order to confirm that magnetic separation is a viable separation method. Solutions of the same concentration of both compositions were mixed and the resulting solution was used for the bimodal separation experiment,
Figure 6-15. Composition dependence response of ferrite nanocrystals to magnetic fields.
This data shows the magnetic field required to retain a specific composition of ferrite nanocrystals. This plot was used to determine the magnetic field needed for bimodal magnetic separation.

We also found that magnetic data collected for these samples in SQUID at room temperature correlate with the percent retention (Figure 6-16.) Zinc ferrite has the highest saturation magnetization, followed my magnetite. Manganese ferrite and cobalt ferrite show a very similar magnetic behavior.
Figure 6-16. Magnetization versus applied field of ferrite nanocrystals. Saturation magnetization data was collected for ferrite nanocrystals in powder at room temperature.

6.4.3. Separation by composition through magnetic separation

For the next experiment, magnetite and manganese ferrite were combined to create a bimodal sample. The bimodal sample was passed through the HGMS at 0.24 T, which retained most of the magnetite nanocrystals, allowing a high percentage of manganese ferrite to pass through in the effluent. This magnetic field was chosen since magnetite has almost reached saturation at this level, thus most magnetite nanocrystals will be retained. The magnetic field was then turned off, 10 mL of hexane were added, and nanocrystals retained in the column were collected. The analysis was performed in three different concentrations, 25, 50, and 100 nM.
of each composition, to observe whether concentration would affect the magnetic separation and it was found that there was no significant difference for different concentrations. Moreover, the ratios of manganese ferrite to magnetite studied were 1:1 and 1:2. The concentrations of nanocrystals were measured with ICP-OES.

In the first experiment at a ratio of 1:1, it was observed that as the bimodal samples was passed through the column with the applied field 72% of manganese ferrite and 89% of magnetite nanocrystals are retained. Once the field was removed, 28% of manganese ferrite and 39% of magnetite nanocrystals were recovered in the first wash with 10 mL of hexane. The rest of the nanocrystals (43% of manganese ferrite and 50 % of magnetite) were recovered in the second wash with 10 mL of hexane (Figure 6-17A).

In a second experiment, a bimodal solution was prepared in a ratio of 2:1 manganese ferrite to magnetite. As the bimodal solution was passed through the column it was observed that 56% of manganese ferrite and 67% of magnetite nanocrystals were retained when the magnetic field was applied. As the magnetic field was removed, 41% of manganese ferrite and 53% of magnetite nanocrystals were recovered in the first wash with 10 mL of hexane (Figure 6-17B). It was observed that in both ratios analyzed, the same percentage of manganese ferrite and magnetite nanocrystals was retained.

A comparison between total concentrations of nanoparticles was also performed at both ratios studied. It was observed that from the total solution at a ratio of 1:1, 80% of nanocrystals were retained in the column. At a ratio 2:1, 66% of
the total solution was retained with the applied field (Figure 6-17C). Finally, Figure 6-17D represents the ratio of manganese ferrite to magnetite used for the studies.

![Graphs](A) (B) (C) (D)

**Figure 6-17. Bimodal separation data of ferrite nanocrystals.**
Initial concentration, concentration of collected nanocrystals with magnetic field on, concentration of collected nanocrystals with magnetic field off, and concentration of nanocrystals collected in second hexane wash for (A) manganese ferrite to mangetite ratio, 1:1, (B) manganese ferrite to mangetite ratio, 1:2, (C) total magnetic nanocrystals (manganese ferrite + mangetite nanocrystals), and (D) ratios between manganese zinc and magnetite nanocrystals.

The data presented here provides a possible method of a composition dependence magnetic separation of ferrite nanocrystals. A different trend in separation was observed for each composition; the method could therefore be
applied to separate different compositions of ferrite nanocrystals from a mixture using HGMS column. While it is not possible to completely separate both compositions at the size (10 nm) at which these compositions were studied, our finding of different percent retentions for each composition is significant. Colvin et al. reported a magnetic separation of a multiplex suspension of varied sizes of iron oxide nanocrystals. Thus, we can conclude that a successful magnetic separation could be achieved using small manganese ferrite nanocrystals (which have a lower magnetic response) and larger magnetite nanocrystals (which have a higher magnetic response). As such, field separation is a feasible biological application for separating more than one type of cells or molecules by composition and size from a complex mixture.

**6.4.4. Conclusions**

Based on the promising findings of a magnetic separation study of varied sizes of iron oxide nanocrystals we performed a composition dependence experiment. First, varied concentrations of nanocrystals were studied and the same retention was seen at concentrations of 100 nM or higher. Therefore, the four compositions were individually studied at a concentration of 100 nM. The percent retention data showed that zinc ferrite has the highest rate of retention followed by magnetite, manganese ferrite and cobalt ferrite nanocrystals. Individual percent retention was utilized to determine the magnetic fields necessary for magnetic separation of a mixed solution.
A bimodal separation experiment between magnetite and manganese ferrite was conducted, which was the first of its kind. These magnetic nanocrystals were chosen since they have distinct retention in an applied field. The bimodal complex solution was passed through the column in a magnetic field of 0.24 T. The data obtained from the bimodal separation showed that the separation of nanoparticles with different compositions is feasible. Although the magnetic separation experiment was performed for nanocrystals at a fixed size, data show that magnetic separation of varied compositions can be achieved selectively by studying different compositions at different particle sizes. This could result in a successful separation of magnetic nanocrystals by composition due to the significant retentions observed. Moreover, an elemental mapping technique with TEM could improve the determination of a successful magnetic separation of varied compositions of magnetic nanocrystals.
References


